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PROCEEDINGS
OF THE
INTERNATIONAL CONFERENCE ON THE PEACEFUL USES OF ATOMIC ENERGY

Volume 8

PRODUCTION TECHNOLOGY OF THE MATERIALS USED FOR NUCLEAR ENERGY

Proceedings of the International Conference

on the

Peaceful Uses of Atomic Energy

Held in Geneva

8 August-20 August 1955

Volume 8

Production Technology of the Materials Used for Nuclear Energy

UNITED NATIONS

New York

1956

UNITED NATIONS PUBLICATIONS

Sales No. 1956.IX.1.Vol. 8

A/CONF. 8/8

Price: U.S. $10.00; 70/- stg.; 43.00 Sw. frs.
(or equivalent in other currencies)

PREFACE

The Proceedings of the International Conference on the Peaceful Uses of Atomic Energy are published in a series of 16 volumes, as follows:

Volume Number	Title	Sessions Included
1	The World's Requirements for Energy; The Role of Nuclear Power	2, 3.2, 4.1, 4.2, 5, 24.2.
2	Physics; Research Reactors	6A, 7A, 8A, 9A, 10A.1.
3	Power Reactors	10A.2, 3.1, 11A, 12A, 13A, 14A.
4	Cross Sections Important to Reactor Design	15A, 16A, 17A, 18A.
5	Physics of Reactor Design	19A, 20A, 21A, 22A, 23A.
6	Geology of Uranium and Thorium	6B, 7B.
7	Nuclear Chemistry and the Effects of Irradiation	8B, 9B, 10B, 11B, 12B, 13B.
8	Production Technology of the Materials Used for Nuclear Energy	14B, 15B, 16B, 17B.
9	Reactor Technology and Chemical Processing	7.3, 18B, 19B, 20B, 21B, 22B, 23B.
10	Radioactive Isotopes and Nuclear Radiations in Medicine	7.2 (Med.), 8C, 9C, 10C.
11	Biological Effects of Radiation	6.1, 11C, 12C, 13C.1.
12	Radioactive Isotopes and Ionizing Radiations in Agriculture, Physiology and Biochemistry	7.2 (Agric.), 13C.2, 14C, 15C, 16C.
13	Legal, Administrative, Health and Safety Aspects of Large-Scale Use of Nuclear Energy	4.3, 6.2, 17C, 18C.
14	General Aspects of the Use of Radioactive Isotopes; Dosimetry	7.1, 19C, 20C.
15	Applications of Radioactive Isotopes and Fission Products in Research and Industry	21C, 22C, 23C.
16	Record of the Conference	1, 24.1, 24.3.

These volumes include all the papers submitted to the Geneva Conference, as edited by the Scientific Secretaries. The efforts of the Scientific Secretaries have been directed primarily towards scientific accuracy. Editing for style has been minimal in the interests of early publication. This may be noted especially in the English translations of certain papers submitted in French, Russian and Spanish. In a few instances, the titles of papers have been edited to reflect more accurately the content of those papers.

The editors principally responsible for the preparation of these volumes were: Robert A. Charpie, Donald J. Dewar, André Finkelstein, John Gaunt, Jacob A. Goedkoop, Elwyn O. Hughes, Leonard F. Lamerton, Aleksandar Milojević, Clifford Mosbacher, César A. Sastre, and Brian E. Urquhart.

The verbatim records of the Conference are included in the pertinent volumes. These verbatim records contain the author's corrections and, where necessary for scientific accuracy, the editing changes of the Scientific Secretaries, who have also been responsible for inserting slides, diagrams and sketches at appropriate points. In the record of each session, slides are numbered in numerical order through all presentations. Where the slide duplicates an illustration in the submitted paper, appropriate reference is made and the illustration does not appear in the record of the session.

Volume 16, "The Record of the Conference," includes the complete programme of the Conference, a numerical index of papers and an author's index, the list of delegates, the records of the opening and closing sessions and the complete texts of the evening lectures.

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Session 14B

TREATMENT OF URANIUM AND THORIUM ORES AND ORE CONCENTRATES

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Recovery of Uranium from Its Ores

By G. Marvin, T. Upchurch, E. Greenleaf, E. Van Blarcom and A. Morphew,* USA

Until recent years, the uses of uranium for all purposes were so small that the requirements were supplied as a by-product of operations for commercial recovery of such metals as vanadium or radium. With the development of applications of atomic energy, demand for uranium increased suddenly and tremendously. Nearly all the uranium obtained during the early phases of our atomic program was produced by process methods which were merely modifications of existing techniques for vanadium or radium recovery. With uranium now the primary product, it became necessary to develop new processes. Any efficient and economical process to accomplish this end necessitated development of means of dissolving the uranium from its ores, and subsequent recovery of the uranium from the solution. Development studies to achieve these objectives were undertaken, not only for the many types of ores found throughout the US, but also for those occurring in many other parts of the world.

Although there are many types of minerals and ores which contain uranium, all of our chemical processing methods involve digestion with either acid or alkaline reagents. The choice between an acid or an alkaline process depends to a great extent on the type of mineralization of the ore under consideration. Uranium mineralization may be of a primary or secondary nature, with uranium being in the reduced state in primary ores, and being in either partially or almost completely oxidized states in secondary ores. Primary ores originating as pegmatites contain the uranium chemically combined with various refractory oxides, for example rare earths, titanium or thorium. These refractory ores require strong acid concentrations to break down the minerals and are not amenable to alkaline leaching. Other primary ores, such as pitchblendes, and all of the secondary ores are amenable to both acid and alkaline processing. With these ores the interference of gangue materials becomes of importance in choosing a process. Calcite, dolomite and magnesite are all serious reagent consumers in an acid process, and their presence may require an alkaline approach. Where the choice of processing methods is not defined by the ore composition, it will depend upon the net effect of several other factors, including reagent costs, materials of construction required, oxidation needed, solubility of undesirable contaminants, the physical handling problems caused by solids or slimes present, and the recovery methods available. In most existing productions plants, acid digestion is the preferred process.

The winning of uranium begins, of course, with the mining industry. In the mining of uranium the usual practices and techniques used for other nonferrous ores apply. After the ore is delivered to the mill, crushing and grinding are required. Here again conventional equipment is needed throughout.

A great amount of study has been undertaken toward development of physical beneficiation methods for uranium-bearing materials, but the results generally have been unsuccessful. Flotation of undesirable gangue materials, such as sulfides, has had some success. Other possibilities include the flotation of a carbonaceous uranium concentrate from asphaltic ores, and flotation of a calcite fraction from high limestone ores. However, in each of these cases the tailings as well as the concentrate must be treated for uranium recovery. Because of the requirement for a low assay in a throwaway tailing, and the presence of several different uranium minerals in the same ore, little success has been achieved.

Other physical methods of beneficiation, such as wet attrition grinding, electrostatic methods, etc., have resulted in either low recoveries or low concentration factors. In summary, only a few of the ores being processed for uranium have been found amenable to physical beneficiation techniques. However, we have no reason to believe that physical beneficiation is not an economic possibility and we are continuing our efforts to develop commercially attractive techniques.

The first step in the chemical treatment of uranium ores in all cases is digestion. Of the two types, acid or alkaline digestion, acid digestion is by far the more widely used technique. We have experimented with the use of various acids to extract uranium and have found nitric and hydrochloric acids to be technically practical, but sulfuric acid has remained the most economical one for our purposes. This is the acid we have used wherever acid processing techniques are employed. The data which I am presenting, while possibly applicable to other acids, have been derived entirely by using sulfuric acid.

In acid digestion, conventional equipment is used throughout the uranium industry. Digestion is accomplished by one of several techniques, such as percolation leach in filter bottom tanks, and mecha-

* US Atomic Energy Commission

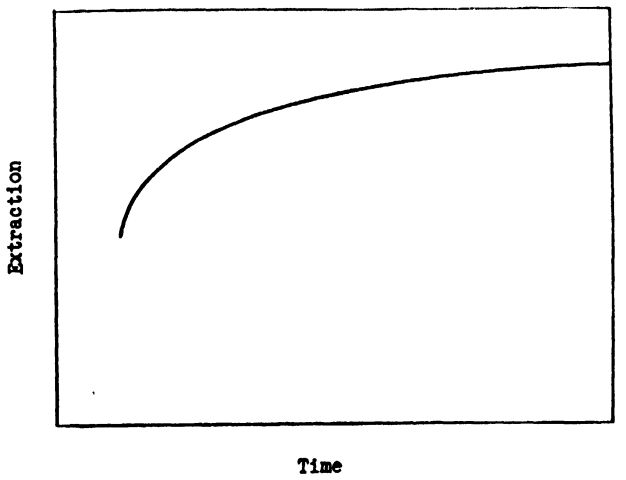

Figure 1. Curve of leaching in an acid system

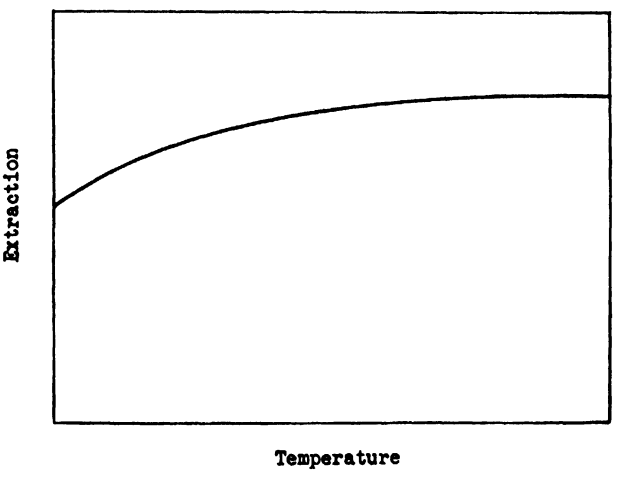

Figure 2. Curve of leaching in an acid system

nical or air agitation leach. Agitation leaching may be either single or multiple stage. Air agitation offers the advantage of adding oxidation effects. In most plants, continuous leaching is used for greater economy. However, in some plants, batch operation is preferred because it offers better control. Where the physical characteristics of the ore permit, advantage can be taken of the relative simplicity of the percolation leach.

Another method of acid digestion that has been used includes the pugging of the ore directly with concentrated acid, which is then allowed to cure for a period of time.

Following this, the ore is leached with water to extract the uranium.

The various conditions of acid digestion have a very important effect on the rate and extent of uranium dissolution. Figures 1 through 4, respectively, show the general relationship of time, temperature, strength of acid, and particle size to dissolution of uranium.

The purpose of these curves is to show in a general way the rate of change of per cent uranium dissolution with change in the variables listed. It is not intended that these charts can be used for any particular ore. For these figures the ordinates represent a range of between 70 and 100% dissolution of uranium. The abscissa of Fig. 1 covers a range of from 1 to 48 hours. On Fig. 2 the temperature ranges between 20°C to 90°C. The terminal acid concentration of Fig. 3 varies from 0 to 20 grams per liter free acid.

On Fig. 4 the particle size diminishes from 10 to 200 mesh.

The use of chemical oxidants during acid digestion is considered to be beneficial to uranium extraction in most cases, and quite markedly so in some instances. For ores in which the uranium is readily acid soluble (over 90% extraction) without an oxidant, the use of an oxidant rarely improves the extraction appreciably. With refractory ores, in which the minerals must be completely broken down to liberate the uranium, or with any ores containing primary mineralizations, and with sulfide-containing ores, the use of an oxidant is required for satisfactory uranium solubilization. There are many oxidants which can be used, but we have found manganese dioxide to be the most economic. Quantities required

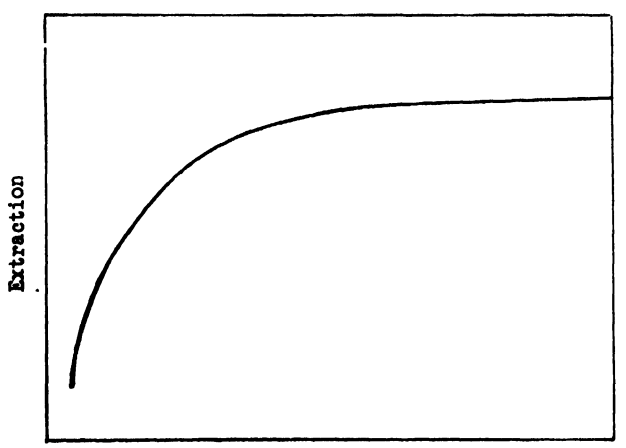

Figure 3. Curve of leaching in an acid system

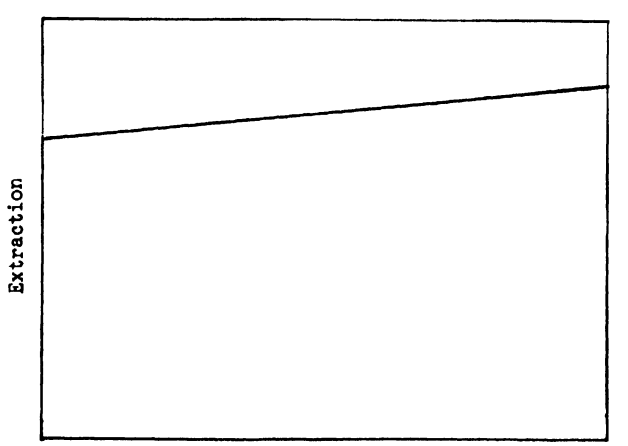

Figure 4. Curve of leaching in an acid system

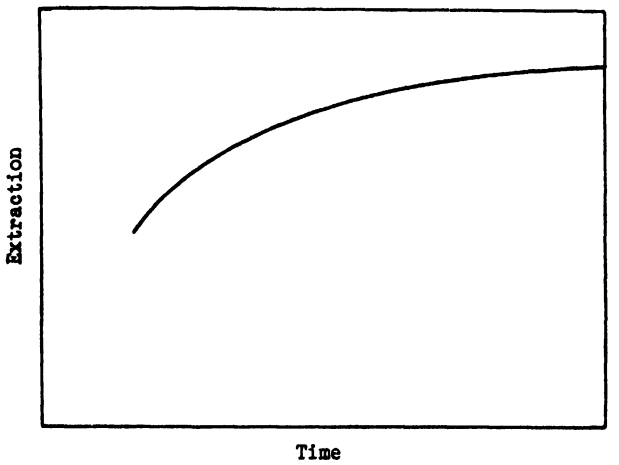

Figure 5. Curve of leaching in an alkaline system

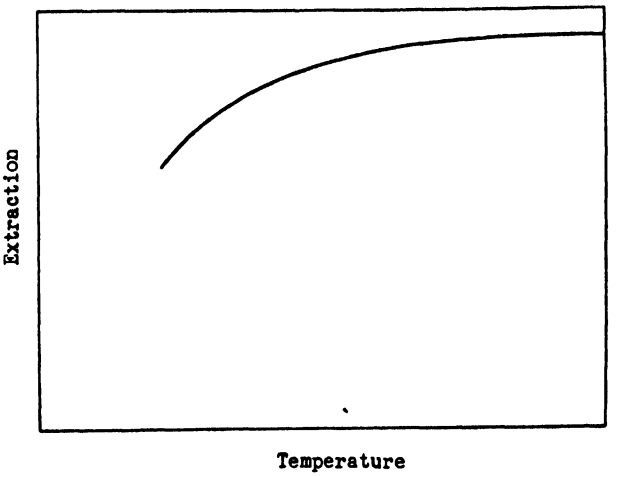

Figure 6. Curve of leaching in an alkaline system

may be in the neighborhood of ten pounds per ton of ore for most ores and higher for very refractory ores.

For those ores which contain large quantities of lime or other acid consuming constituents, the economics of acid digestion usually are unfavorable. Therefore, we use alkaline reagents to extract the uranium. We have investigated a number of these reagents including sodium carbonate, sodium bicarbonate and ammonium carbonate. To date, the most useful alkaline reagent has been a mixture of sodium carbonate and sodium bicarbonate. The purpose of the bicarbonate in the mixture is to prevent any increase in pH of the leach liquor during extraction, because the uranium will precipitate if the pH becomes too high. In the digestion step of an alkaline process, conventional types of equipment and materials of construction are employed. We have found the use of either mechanical agitation or Pachucas to be quite effective. Pachucas have the advantage of permitting operation at temperatures above the normal atmospheric boiling point. Another means of achieving this effect, applied only in extreme cases, is the use of autoclaves. These techniques can be employed either in batch or continuous operation. Figures 5 through 8, respectively, show the relationship of time, temperature, strength of reagent and particle size to uranium dissolution. For these figures for carbonate leaching conditions, all ordinates again represent a range of from approximately 70 to 100% dissolution of uranium. Figure 5 has a time range of from 4 to 96 hours. The temperature range for Fig. 6 is roughly 20°C to 90°C. Figure 7 represents a carbonate concentration range of from 20 to 150 grams per liter, combined sodium carbonate and sodium bicarbonate, expressed as sodium bicarbonate. Particle size range of Fig. 8 diminishes from 10 to 200 mesh. In general, uranium extraction by alkaline reagents has not been as good as with acids. However, through the use of improved operating technology, we have been able to increase the efficiency until it approaches that of acids. Carbonate leaching offers the additional advantage over acid leaching that lesser amounts of undesirable constituents are dissolved.

In a carbonate system, oxidation is generally more critical than in an acid system because of the fact that uranium must be in an oxidized state in order for dissolution to occur in a carbonate system. The amount of oxidation required must be determined

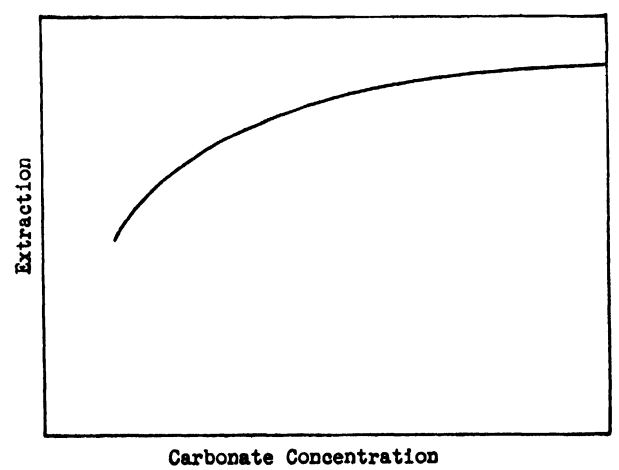

Figure 7. Curve of leaching in an alkaline system

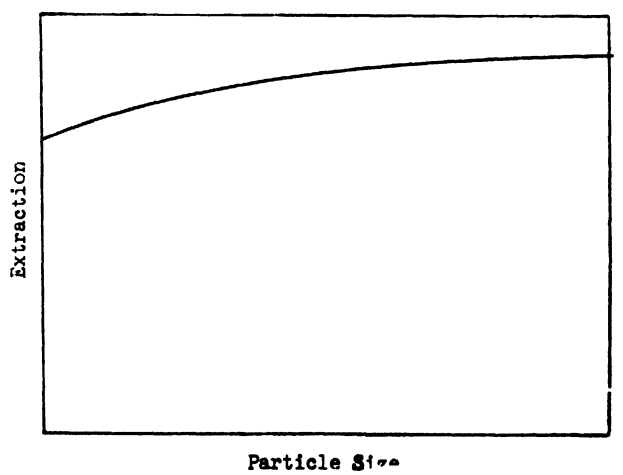

Figure 8. Curve of leaching in an alkaline system

for each ore but in general depends on the amount of reduced uranium mineralization present in the ore. In an atmospheric digestion system, nothing has been found which will approach potassium permanganate for ability to improve extraction from refractory ores; however, in a pressure system air oxidation will approach the performance of permanganate in an atmospheric system. For ores which require little oxidation, air oxidation of the digest slurry at atmospheric pressure may be sufficient to achieve acceptable extraction.

I now have discussed two major approaches to dissolving uranium from its ores. There is nothing particularly unique about the methods used in either approach to get the uranium into solution. However, for efficient recovery of uranium from digest solutions, the problems of effecting solid-liquid separations were so great in many cases that techniques not previously used in the metallurgical industry had to be developed. Originally, our conventional chemical precipitation techniques required a clear liquor in order that the final uranium concentrate would not be contaminated with entrained solid material. However, as uranium ores of different origin were encountered, thickening and filtration of slimy solids became a serious difficulty. This led to the development of recovery techniques which could be performed in liquors that had undergone simply a sand-slime separation or in slurries direct from the digestion tanks. The choice of one method over another depends entirely on the overall economics for a particular ore. Techniques employed for clarifying or desanding liquors are conventional hydrometallurgical processes and selection of a particular type of equipment is governed by the characteristics of the ore involved.

It has been found that roasting certain ores sometimes has a significant effect on uranium solubility and the handling characteristics of the ore. In many cases the filtering and settling rates of untreated ores are so slow as to be almost prohibitive. In such cases thermal treatment in conventional roasters improves filtering and settling rates, sometimes significantly. Fortunately, most ores do not require this treatment. Care must be observed to avoid over-heating in thermal treatments as this may reduce the uranium solubility.

Recently new chemical flocculents have become available commercially which effect marked improvement in thickening or settling the slurries from digestion. In some cases, they assist clarification so greatly as to affect the choice of solids handling equipment or techniques, or to eliminate the need for roasting.

Uranium recovery from digest pulps or liquors can be accomplished by four principal methods, namely: chemical precipitation, static bed ion exchange, fluidized bed ion exchange and organic solvent extraction. Each of the above techniques may be used for either acid or alkaline leach pulps.

The simplest procedure is straight chemical precipitation. This requires first of all complete clarification of the leach liquor, then the addition of the precipitating agent. The advantages of this method are simplicity and straightforward operations employing conventional solid-liquid separation equipment, precipitation tanks and filtration of final product. It can be used only on ores which can be readily clarified. It has the disadvantage of high cost in the case of acid digestions, because of the high consumption of reagent needed to neutralize all the acid present. In addition, the barren leach liquor usually is not useful for recycle after neutralization. An alternate method is to precipitate uranous phosphate, by the reduction of the uranium to the uranous (+4) valence, followed by addition of phosphate. This method does not destroy all of the acid values, and some recycle is possible.

Chemical precipitation is more commonly used in alkaline than in acid systems. When a leaching mixture of sodium carbonate and sodium bicarbonate is employed, uranium can be recovered from a clarified leach liquor by the use of alkali to raise the pH to the point of uranium precipitation. The barren leach liquor can be regenerated by the use of CO_2. The carbonate-bicarbonate ratio can be adjusted by the addition of small quantities of sodium bicarbonate. A continuous bleed-off is required to prevent build up of interfering constituents. Other methods which have been investigated for recovery of uranium from alkaline solutions include hydrogen reduction, sodium amalgam reduction, and electrolytic reduction. While the main advantage of these methods is that they permit recycle of chemical reagents, none of them is in use at present because of insufficient development.

The use of ion exchange resins has been widely adopted for recovery of uranium from sulfuric acid leach liquors. In using ion exchange resin columns the pregnant liquor must be clarified. This process utilizes modified water softening equipment which consists of large columns containing beds of ion exchange resins. The clear pregnant solution is passed through this bed of resin until the resin is loaded with uranium. The resins most commonly used are of the anion type and are commercially available. After the loading cycle has been completed and the bed adequately washed, the uranium is removed from the resins by the use of mixed solutions of ammonium nitrate and nitric acid. Other eluting solutions are possible, but at present these are the most satisfactory. Conventional ion exchange technology is practiced. Modifications are made as needed to fit the peculiar characteristics of uranium adsorption and elution and to provide for the removal of impurities. A precipitate is recovered from the eluting solution by the addition of ammonia or other basic compounds, such as magnesia. This precipitate is filtered and dried sufficiently for shipment. While we have no ion exchange columns in production on alkaline leach liquors, we know the method is technically possible.

The development of the ion exchange technique was significant to uranium recovery in that it represented the first departure from conventional hydro-

metallurgical methods. The advantages that are inherent in this approach are that we now have a method which greatly concentrates the uranium in solution; that is, the uranium concentration in the dilute acid leach runs in the range of ½–1 gram per liter as compared to the concentration in the ion exchange eluate of 10–20 grams per liter. At the same time, the concentration of other elements which normally coprecipitate with uranium in a chemical precipitation are decreased or eliminated and, therefore, not precipitated from the eluate with the uranium product. Thus, we have an economic method which yields a high grade product directly without any intermediate up-grading steps.

A modification of the ion exchange technique to eliminate the requirement that feed to the resin be water clear, was developed for use on ores that have difficult thickening characteristics. This is a fluidized-bed-ion-exchange technique known as resin-in-pulp. The chemical characteristics of the resin used are the same as for the resins used in columns. However, the particle size is considerably larger. These larger particles of resin are placed in a perforated stainless steel basket which has openings smaller than the resin beads, but larger than the particles in the pulp fed to the process. The acid leach liquor from the digestion tank first passes through the sand-slime separation to remove the coarse sands. The desanded pulp is then fed into a series of cells containing baskets partially filled with the ion exchange resin. The baskets are operated by an overhead drive which slowly moves them up and down in the solution. By this means, the resin beads are kept in motion while suspended in the pulp. This motion is to insure efficient contact between the resin beads and the uranium in the pulp. The barren pulp from the process may be discarded, thus eliminating a costly and difficult solid-liquid separation step. The uranium-loaded resins are then eluted in a manner chemically the same as for resins in columns. As the eluting solution progresses from one cell to another, the baskets continue to move up and down, to keep the resin beads in motion. The uranium is precipitated from the eluting solution in the same manner described above for ion exchange columns. This process will be employed in a number of plants which are now under construction. We also are developing a technique for using resin-in-pulp to recover uranium from alkaline solutions. This work has progressed quite satisfactorily but is not in full scale production at present.

The fourth technique I will describe for recovery of uranium from solutions utilizes organic solvents. To date, use of this method has been confined to acid solutions. We have plants under construction and in operation utilizing this technique to recover uranium from phosphoric acid. In addition, development work has progressed through the pilot-plant stage applying the method to ores from the Colorado Plateau region.

The extractants which have been most successfully used in this technique are esters formed by the reaction of phosphorous pentoxide with straight or branched chain alcohols of eight or more carbons. These extractants generally are used in diluted form, in a diluent such as kerosene. Depending upon the particular characteristics of the digest slurry involved, strengths of organic extractants ranging from 2 to 10% might be employed. Other extractants are being investigated.

The original application of solvent extraction was on clear solutions. Recently the technique has been adapted successfully to leach slurries. The coefficients are sufficiently high that quite efficient extraction may be expected in a very few stages. The organic and pregnant aqueous phases are contacted by mixer-settlers or columns, such as are used in conventional extraction. On an experimental basis we have investigated pulsed columns and centrifugal contactors.

The chief difficulties encountered in solvent extraction have been the occurrence of emulsions and the loss of organic extractant in the raffinate. With proper choice of equipment and operating conditions they usually can be avoided or controlled. After the organic solvent has been separated from the leached liquor, the uranium may be stripped in a number of ways depending upon the extractant used. Hydrofluoric acid has been used successfully to form uranous tetrafluoride, which is a final product. Other stripping agents, such as hydrochloric acid, are desirable when they can be used.

Limited study has been made on processes whereby the ore is contacted with an organic solvent free of a water phase. The ore may or may not have received an acid cure, and the solvent may or may not contain a mineral acid. Separation of loaded solvent from the residue is generally quite simple and recovery of uranium from the organic is similar to procedures described previously.

By any of the techniques which I have described, the uranium is in precipitated form, which then is filtered and dried for shipment. The product grade usually is 70% or better. Overall recovery by ion exchange resin-in-pulp is better than 90% from both alkaline and acid solutions. Costs of the final product are considerably less than for the material produced by the original techniques adopted from vanadium and uranium technology. Moreover, we are constantly improving our practical skill through operating experience to give even better yields and lower costs.

This paper has been a summary of all the steps which we employ to produce uranium from the ores now being treated. Of necessity it was not possible to describe technical details. These you will find in the papers in the proceedings of this session.

Principles and New Developments in Uranium Leaching

By A. M. Gaudin,* USA

In this paper our objective will be to examine the developments in uranium leaching in the post-war decade so as to bring out the significant features rather than the details of this art.

Before 1940 uranium leaching was carried out primarily on the yellow or carnotite-type minerals. It was generally a small-scale, batch operation, primarily designed to recover vanadium or radium with uranium as by-product.

The atomic age has changed this radically. Uranium is now the principal constituent. Associated metals such as vanadium, radium, cobalt, silver and even gold have become increasingly incidental to the recovery of uranium. Processes and flow sheets have had to be altered to implement this basic change. The greatly enhanced value of uranium has made lower-grade ores economically acceptable. This in turn has greatly increased ore reserves and has made possible the development and use of *continuous leaching processes.*

Since the ores treated have been lower grade, large-scale operations have become possible, with further lowering in the grade of uranium that is acceptable in an ore. Accordingly entirely *new standards of analytical accuracy* have become imperative for the purpose of operative control of the leaching operations. If it be assumed that uranium oxide in the form of a high-grade product from leaching is worth as much as silver, a raw material containing 0.10% U_3O_8 becomes ore under the prevailing general economic conditions. And if recovery in a given operation must be known to the nearest one per cent of the recovery, the analytical methods must be such as to analyze for one part per 100,000 in the residue and for even lesser concentrations of uranium in spent liquors.

These two major requirements for uranium leaching operations, namely continuity of processing and highly accurate process control, are among the most important of overriding attributes of suitable operation. Two other important factors are the selection of a process employing *relatively non-corrosive leach liquors,* and the *use of ambient temperature* in lieu of deliberate heating. Non-corrosive leach liquors are clearly desirable especially when the service on the capital investment for a Uranium Reduction Works becomes an increasingly large proportion of the total cost of producing the metal. Use of ambient temperature in place of elevated temperature results in operating economy, the saving being increasingly large, percentage-wise, as the grade of ore is lowered.

URANIUM MINERALS

Uranium minerals fall into three classes of which two are important sources of metal. In one class uranium occurs as the oxides uraninite and pitchblende and is largely in the tetravalent state. In the second class uranium occurs as hexavalent compound salts with other metals, or simply as the hexavalent oxide or hydrated oxide. And in the third class it occurs in tetravalent form as a mixed oxide with other metals such as titanium, thorium, columbium. This third class is at present relatively unimportant and will not be considered further in this paper. Uranium ores for our purpose, therefore consist of the black ores with uranium largely tetravalent and the yellow (and green) ores with uranium largely hexavalent.

Tetravalent uranium minerals seem to have required reducing conditions for their formation. They are generally associated with reducing agents such as hydrocarbon minerals, graphite, native metals and sulfide minerals. Hexavalent uranium minerals normally display no such associations.

NEED FOR OXIDIZING AGENTS IN LEACHING

Compounds of hexavalent uranium are much more soluble in water than those of tetravalent uranium, and they more frequently form water-soluble complexes. To dissolve uranium minerals it is therefore necessary to provide an oxidizing agent whenever the uranium occurs in tetravalent form, or in the rare cases where a hexavalent uranium mineral is in close association with active reducing minerals. This *provision of an oxidizing agent* may be termed the fifth important requirement for uranium leaching. According to circumstances the oxidizing agent may be manganese dioxide, ferric iron, chlorine or chlorate ion.

Manganese dioxide is outstandingly effective in acid circuits (Table I).

And where manganese compounds are valuable, it may sometimes be recovered at a later stage of the process by precipitating manganous hydroxide, and then oxidizing the precipitate with atmospheric oxy-

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Table I. Effect of MnO_2 on Dissolution of Uranium from a Siliceous Ore in which Part of the Uranium Occurred as Pitchblende (acid constant)

MnO_2 lb/ton ore	Uranium extraction, %
0	88.0
5	92.3
15	95.2
30	95.6
50	96.5

gen. In some experiments the conversion of Mn^{++} to MnO_2 ranged from 60 to over 90% according to the temperature and duration of the oxidation, the best results being obtained by roasting at about 300°C

Ferric iron is useful, except for the fact that it introduces an element sufficiently similar to uranium in regard to chemical properties to make later steps of recovery somewhat more difficult. So, in general, ferric iron is not added to the system although some of it seems invariably present in practical leach liquors.

Chlorine, chloride of lime and chlorate ion all are effective in acid circuit, but they produce chloride ion which is definitely corrosive to steel in acid circuits. It is therefore preferable to avoid it. To date atmospheric oxygen has not been found effective in acid circuits as a uranium oxidizer, but the matter needs perhaps additional study. Permanganates, bromine, hydrogen peroxide and other oxidizing agents familiar to the analytical chemist are useful but practically unsuitable because of high cost.

Ascertainment of proper addition of oxidizer during leaching may be made by an empirical potentiometric method. This consists in measuring the potential across a pair of electrodes (platinum-calomel) immersed in the slurry. The potential changes primarily in accordance with the relative abundance of ferric to ferrous iron, but modifications in the numerical e.m.f. are introduced if elements other than iron are present in substantial concentration, these elements being characterized by the assumption of many valencies. Vanadium is conspicuous in this capacity.

URANIUM SOLVENTS

Among solvents for uranium minerals, sulfuric acid and sodium carbonate have been found especially practical. Sulfuric acid leads to formation in solution of uranyl sulfate, UO_2SO_4, which ionizes not only to give uranyl cation UO_2^{++} and sulfate anion SO_4^{--}, but also uranyl sulfate complex anions, $UO_2(SO_4)_3^{4-}$ and $UO_2(SO_4)_2^{=}$. The dissolved uranium occurs in all three forms simultaneously, the abundance of these forms being controlled by complex equilibria involving the concentrations of hydrogen, sulfate and bisulfate ion besides that of the various forms dissolved uranium. In the same way sodium carbonate leads to formation in solution of the complex uranyl carbonate anion, $UO_2(CO_3)_3^{4-}$. The sodium carbonate process is inherently more selective than the sulfuric acid process. This is because nearly all metal carbonates except the alkali carbonates are insoluble in water and do not form complexes. On the other hand the dissolution of uranium minerals in carbonate solutions is slow, elevated temperatures are needed for the attainment of a reasonable leaching rate and the process is finicky in regard to the proper proportioning of carbonate to bicarbonate ion. Finally, the concentration of carbonate and bicarbonate ions in the solutions must be high. Accordingly, the process must be cyclic in regard to carbonate. In general when the uranium is hexavalent and if the gangue minerals include a substantial proportion of alkaline-earth carbonates, the soda ash process should be used. When the gangue is siliceous the sulfuric acid process is preferred, especially if the uranium is in part at least in tetravalent form.

Other solvents for uranium have been suggested including nitric acid, hydrochloric acid and potassium carbonates. These solvents, however, offer no advantages over the cheaper sulfuric acid and sodium carbonate. The one exception might be nitric acid which would appear peculiarly well suited in conjunction with ether or like material in a solvent-extraction step.

Dissolution of uranium minerals in an aqueous solvent is but the first step in the leaching process. Two broad classes of processes are used for the subsequent recovery of the dissolved uranium. In one category, the pregnant liquor is separated from the spent residue and the uranium is extracted from the liquor. In the second category there is no separation of pregnant liquor but rather direct removal of uranium from the liquor while in presence of the spent residue.

SOLID-LIQUID SEPARATION

The first kind of process clearly involves the same unit operations that are currently employed in the recovery of gold by cyanidation. These unit operations include thickening and filtration. Thickening and filtration are more expensive and technically more difficult to apply in acid uranium leaching than in cyanidation. If the solvent for uranium is an acid, the residue must be settled in acid liquors rather than in gently alkaline water. Silicate minerals, particularly clays, are more difficult to flocculate in these liquors than in lime water so that the thickeners have to be larger. Alternatively, special flocculants have to be used. Among these special flocculants may be mentioned certain polyelectrolytes similar to those which have been developed for soil conditioning. If filtration is used, the capacity of the filters in the uranium operations is reduced as compared with their capacity in cyanidation for gold, and more units have to be employed to do the job. Furthermore, the filters as well as the thickeners have to be acid-proofed. In the soda ash process, filtration and thickening problems are relatively simple both because the pulp is hot and because it is alkaline. This is one

of the major advantages of the soda-ash leaching method.

PRECIPITATION METHODS

For the separation of uranium from the pregnant liquor, five different methods have been used. These are: *precipitation, reduction followed by precipitation, electrolysis, adsorption on anion-exchange resins and solvent extraction.*

Precipitation of uranium carries over into uranium leaching a unit operation familiar in leaching for other metals. In the case of aluminum metallurgy for example, the pregnant solution from the leaching of bauxite by sodium hydroxide in the Bayer process is precipitated by reducing the alkalinity or by cooling. In the same way uranium can be precipitated using an alkali, or fluoride ion, or phosphate ion, or with hydrogen peroxide. These precipitates can be made quantitative when the solutions are reasonably concentrated so that the spent liquor can be discarded if it is not valuable for other reasons. On the other hand the precipitation processes are not really selective enough in dealing with sulfate liquors. Iron, in particular, is troublesome when the hydroxide precipitation is attempted. To utilize precipitation to recover uranium from leach liquors and at the same time to separate uranium reasonably well from iron requires boiling of the muddy ferric hydroxide precipitate. This operation promotes the dehydration of the ferric precipitate and reduces the uranium carried with it. Precipitation with hydrogen peroxide gives a pleasantly granular uranium product but requires purification of the pregnant liquor and this is an onerous requirement. Finally, the process demands a substantial excess concentration of hydrogen peroxide for completion of precipitation so that it is of doubtful value with dilute liquors. Phosphate and arsenate precipitation not only introduce undesirable impurities in the product but are also difficult to carry out without prior purification of the liquor.

Precipitation recovery of uranium is often spectacularly improved by reduction. In the case of acid liquors this can be done by passage over zinc amalgam, aluminum or iron, precipitation of the reduced uranium resulting from addition of phosphate, arsenate or fluoride. In the case of carbonate liquors the reduction and precipitation can be effected simultaneously by hydrogen reduction over a nickel catalyst at elevated temperature and pressure.

Table II gives an indication of the grade of precipitate and of the precipitation recovery obtainable from a typical acid liquor.

CYCLIC ELECTROLYSIS

The third method by which uranium may be removed from pregnant solutions has been especially useful in dealing with carbonate solutions. It will be recalled that carbonate leaching requires careful balance of carbonate to bicarbonate ion. A deficiency of bicarbonate (at same carbonate plus bicarbonate) makes it much more difficult to leach the uranium. It is believed that this is to be traced to the concomitant increase in the hydroxyl ion concentration. Conversely, precipitation of dissolved uranium from carbonate solutions is easily obtained provided the pH is increased. This can be done elegantly in an electrolysis cell having two compartments separated by a porous diaphragm. Bicarbonate is generated at the anode and hydrous sodium diuranate is precipitated at the cathode. A cyclic process can then be arranged resulting in substantially complete reuse of carbonate without necessity for a large bleed with which to discard added electrolytes. The problems that remain in such a process are the freeing of spent residue from entrained carbonate and the practical carrying out of operations at elevated temperatures.

Table II. Grade of Uranium Precipitate and Precipitation Recovery From a Sulfuric Acid Leach Liquor Containing 0.32 gm U_3O_8 per liter

Precipitation method	*Grade, % U_3O_8*	*Precipitation recovery, %*
Neutralization with magnesia	3.1	99+
Neutralization with magnesia, filtration of precipitate, acid digestion at pH 3.5, second filtration and precipitation of filtrate with hydrogen peroxide	86.8	96.1
Reduction of liquor followed by phosphate precipitation	69.8	98.7

ANION EXCHANGE RESINS

To date the most widely used process for removal of uranium from solution involves the use of anion-exchange resins. These resins can be likened to a three-dimensional coat hanger in which the hooks are all occupied by anions willing to trade places with less labile anions such as sulfate, bisulfate, uranyl sulfate complex anions, etc. When the pregnant liquor is passed over a column of beads of ion-exchange resin, the exchangeable ions in the resin diffuse outward in each bead while the exchanging ions in the liquor diffuse into each bead. Eventually all the "hooks" in the resin are occupied by the most tenacious ion. It happens that resins are available, such as IRA-400, Dowex 50, Permutit SK, which will preferentially extract uranium sulfate complex ions and uranium carbonate complex ions over all the other ions mentioned so far. For example, these uranium-bearing ions will displace chloride, nitrate, sulfate and bisulfate ions.

When the ion exchange resin is saturated with uranium, the adsorption process is reversed. This is done by passing over the resin bed a new solution called the eluant in which the concentration of the ion that has been displaced on the resin by the uranium-bearing ion is drastically increased. This causes uranium, practically alone among heavy metals, to appear in the eluate from which it is easily recovered by simple precipitation. This precipitation is facilitated by the relatively high uranium content of a properly engineered eluate.

The process is continuous and yet intermittent in the sense that one column of resin is first exposed to a relatively large volume of pregnant solution, then washed, then exposed to a relatively small volume of eluant, then washed again before the cycle is resumed. Several columns are therefore employed so as to have some on elution while others are on the earlier step of exhaustion.

Ion-exchange resins have proved themselves satisfactorily long lived. The mechanical deterioration of the resin beads that was at first feared was not encountered. On the other hand, certain ions have occasionally created difficulties. The exact form of these aggravating complications is not completely understood and is still under study; however, some progress has been made in identifying the offenders and in counteracting them. For example, a resin which had been used on acid leach liquors on a Rand ore showed 3.34% S, 5.19% SiO_2 and 2.68% Co when received for study. The uranium capacity was only 31.5 grams U_3O_8 per liter of wet settled resin against 70 grams in fresh resin. Purging with sodium hydroxide removed the silica without changing either sulfur or cobalt, increasing the resin capacity to 37 grams. Alternatively purging with sodium sulfide and sodium hydroxide reduced the sulfur to 0.5%, removed the silica, and increased the capacity to 40 grams. A second purging with ammonium thiocyanate removed the cobalt, too, and increased the capacity to 51 grams per liter.

SOLVENT EXTRACTION

The last process for removal of uranium from pregnant liquors is the solvent extraction process. In this process an organic liquid is contacted with the pregnant solution, the organic liquid being selected so that it will offer a more attractive environment than the aqueous solution for a non-ionized uranium compound. Thus, a pregnant solution containing nitrate ion contains also a small but not inconsequential concentration of undissociated uranyl nitrate molecules. This form of uranium is very soluble in ether containing nitric acid. Accordingly, when an organic phase of the right composition is contacted with the pregnant solution, uranium passes from the water into the organic liquid almost without impurity. The reduction of non-ionized uranyl nitrate in the aqueous phase is immediately compensated by association of uranyl with nitrate ions in the water in accordance with the well-known principles of mass action, and the extraction of uranium from water to organic liquid proceeds until equalled by back-extraction. The process can be made complete by design of a solvent extraction operation consisting of more than one step, arranged counter-current fashion.

After separation of the phases the organic liquid containing uranium is backwashed with water containing ions at other concentrations than the original pregnant solution. Under these circumstances uranium backwashes into the new aqueous phase in a practically pure form; it can be removed from this dissolved state, for example, by precipitation with ammonia. Although the process has been described here as using ether as the organic liquid, other solvents are also suitable, such as hexone, or a mixture of kerosene with tributyl phosphate, tri *n*-octyl amine, or dodecyl phosphoric acid.

The solvent extraction process has been found suitable for the recovery of uranium occurring in minute quantities in the phosphoric acid made from phosphate rock.

RIP AND SIP PROCESSES

It was indicated above that if a uranium extraction process of the second category was employed, it was *not necessary to separate the pregnant solution from the residue* prior to uranium extraction. Two methods for doing this have been used, one employing anion-exchange resins and the other solvent extraction. The anion-exchange or resin-in-pulp (RIP) processes involve the moving, counter-currently, of an ion-exchange resin and the ore pulp. The spent liquor and suspended residue come out at the place where the fresh resin enters and the uranified resin comes out where the leached ore pulp arrives. Several methods have been developed for this counter-current movement of resin and pulp. Most methods depend on confining the resin inside of a container that has pores small enough to retain the resin but large enough to allow as free passage as possible of the pulp solids. Development of processes in which the resin is not in a container is desired, and of course work is being done in this field at present.

In the application of solvent extraction to leached pulps a great opportunity is offered for improving on the operation of the usual solvent extraction. This advantage arises from the fact that the relative volume of water to organic phase during the exhaustion of the pregnant liquor can be reduced by one or two orders of magnitude. Thus, instead of conducting the process of leaching with four parts of water to one part of ore, it can perhaps be carried out with one-fifth part of water to one part of ore. This gives a twentyfold advantage to the step of extracting the uranium by the solvent. With the same volume of solvent more attractive partition can be obtained; or, alternatively, a solvent giving a less desirable partition coefficient may be selected, its other advantages (such as non-flammability or cost) receiving more weight.

The solvent extraction process in pulp (SIP) can in fact be conducted under conditions where the aqueous phase is just abundant enough to wet the solids, causing them to adhere to each other, forming plastic granules or balls and permitting to avoid entirely the necessity of conducting a difficult separation of spent solids from pregnant solution.

With both of these processes the ultimate step of recovering the uranium from ion-exchange resin or from the solvent is of course the same as in those cases where the spent waste solids are first separated from pregnant liquor.

PRECONCENTRATION

To round out the application of leaching to the extraction of uranium, it is appropriate to suggest that combination of leaching with preconcentration may be advantageous. In some instances heavy media or other gravity separating methods can be employed to reduce the quantity of ore to be treated for the same uranium production. In other cases flotation preconcentration can be used. This is a rather new use of the flotation process which in general is regarded as the ultimate process in a concentration operation. Here it is viewed primarily as a preconcentration procedure yielding feed for a leaching plant. Still another use of flotation preconcentration is in connection with ores containing a considerable proportion of carbonate minerals. These minerals can be floated off without regard to the uranium distribution, the flotation froth going to a carbonate leaching plant and the flotation non-float to a sulfuric acid leaching plant.

SUMMARY

To summarize, the new ideas that have changed the technology of uranium leaching since the war are the following: (*a*) use of continuous leaching in place of intermittent leaching; (*b*) development of vastly improved analytical methods; (*c*) use, when possible, of ambient temperature; (*d*) choice of liquors as non-corrosive as possible for the mill equipment; (*e*) employment of an oxidizing agent where reduced uranium minerals occur or where uranium minerals are mixed with reducing minerals; (*f*) development and application of new processes for extracting uranium from the pregnant liquors, including cyclic electrolysis, adsorption on anion-exchange resins and solvent extraction; (*g*) invention of processes (RIP and SIP) that avoid the costly step of separating spent solids from pregnant liquor; and (*h*) combination of leaching with preconcentration processes.

ACKNOWLEDGEMENTS

It is a pleasure to record the assistance in the preparation of this manuscript of Mr. D'Arcy George, Mineral Engineer, and Miss Beulah Leacy, Librarian, National Lead Company, Winchester, Massachusetts. It is appropriate to record that much of the progress made in the field of uranium leaching which is sketched here was made by staffs of the Richards Mineral Engineering Laboratories of the Massachusetts Institute of Technology, the American Cyanamid Company, Stamford, Connecticut, and the National Lead Company. The inspiring cooperation of atomic energy agencies at other United States Laboratories and overseas is also gratefully recognized particularly of the Dow Chemical Co., Pittsburg, California; Arthur D. Little, Inc., Cambridge, Massachusetts; the Battelle Memorial Institute, Columbus, Ohio; the Eldorado Mining and Refining Company and the Canada Department of Mines and Resources, Ottawa, Ontario; the United Kingdom Laboratories at Harwell and Teddington; the Government Metallurgical Laboratories, Johannesburg, Union of South Africa; and the Council for Scientific and Industrial Research, Melbourne, Australia.

In connection with the research work on uranium leaching, the author is indebted to and acknowledges gratefully the cooperation of Mr. John Dasher (Chemical Construction Company), Dr. C. F. Davidson (UK Geological Survey), Mr. Dan Kentro (United States Atomic Energy Commission), Dr. Philip Merritt (E. J. Longyear Company), Professor R. Schuhmann, Jr. (Purdue University), Professor Leonard Taverner (University of the Witwatersrand), and Mr. Arvid Thunaes (Eldorado Mining and Refining Company).

Some Unusual Problems Met in the Recovery of Uranium from a Very Low-Grade Ore

By M. D. Hassialis and R. C. Musa,* USA

The Chattanooga shale formation is divided into five lithologic units designated by Conant[1] as Top Black shale, Upper siltstone, Middle Black shale, Middle Grey siltstone, Lower Black shale and termed by Stockdale [2] simply as E, D, C, B and A respectively. The Gassaway member which is comprised of units C, D and E and is about 17 ft thick has been examined as a potential uranium ore. A typical mineralogical composition as determined by Bates[3] is given in Table I. Its uranium content is extremely low ranging from 0.005–0.0065% U. As a direct consequence of this very low grade a systematic search for beneficiation methods encounters unusual problems, some of which are completely novel while others are problems which normally have no practical significance with higher-grade ores.

A common point of departure in the search for ore-dressing methods is knowledge of the mineralogy with particular emphasis on the uranium minerals and their dissemination throughout the ore. In the case of the Gassaway member the dissemination is so fine that no uranium minerals have been isolated or identified. To resolve this difficulty statistical techniques were used to establish the existence of associations in geometry or behavior between the uranium and the other minerals of the shale.

Application of the method involves the production of samples of shale exhibiting variations in uranium content and variations in the other variables with which association is to be established. Typical are the samples given in Table II which were produced by passing a sample of Top Black shale through a micronizer set to give — 20-micron material which was then infra-sized into a number of settling-rate fractions. Each product was assayed for uranium, pyrite and carbon with the results given in columns 2, 3 and 4. It should be noted that figures given for pyrite are somewhat unreliable since the inconsistency of X-ray analyses forced the use of a chemical method based on the acid solubilities of the various iron-bearing minerals. Total iron is determined by digesting the sample with HF-HNO_3. Soluble iron is determined by digesting 100 mg of sample for ½ hr with 10 ml of 1 : 1 HCl and 5 ml of 1:1 H_2SO_4, then filtering, washing residue with 100 ml of hot water and determining iron colorimetrically on an aliquot of the filtrate. Pyrite-marcasite is determined by treating the above residue with 15 ml of 1 : 1 HNO_3 for ½ hr, filtering, washing with 250 ml of hot water and determining iron colorimetrically on an aliquot of the filtrate. As a check, a second residue is digested with 10 ml of conc. HCl and 5 ml conc. HNO_3 for ½ hr, filtering, washing with 250 ml of hot water and testing an aliquot of the filtrate. The HNO_3 and aqua regia results should agree within 5% or less.

If U, C, P denote the uranium, carbon and pyrite assays respectively, $\overline{C}$ and $\overline{P}$ the mean carbon and pyrite assays, a the uranium content when C and P are at their means, while b_1 and b_2 denote the rates of increase of U with C and P when P and C are held constant, then assuming a linear relationship between U, C and P we may write

$$U = a + b_1(C - \overline{C}) + b_2(P - \overline{P})$$

This may be rewritten as

$$U = d + b_1C + b_2P \qquad (1)$$

where $d = a + b_1\overline{C} + b_2\overline{P}$. Using the standard methods[4] of multiple correlation, the following partial correlation coefficients were obtained:

0.85 = correlation coefficient of uranium with carbon, pyrite being held constant.

0.33 = correlation coefficient of uranium with pyrite, carbon being constant.

The latter coefficient is not statistically significant. This is more apparent if the constants are put into Equation 1 together with their 95% confidence limits. There results

$$U = (0 \pm 20) \times 10^{-4} + (5.2 \pm 1.3) \times 10^{-4}C + (1.0 \pm 1.0) \times 10^{-4}P \qquad (2)$$

It follows that 60–100% of the uranium is associated with carbon and, since 99% of the carbon in shale derives from kerogen, the association is with kerogen; 0–28% of the uranium is associated with pyrite; and 0–25% is associated with material other than kerogen and pyrite, i.e., the silicates and clays. The proper conclusion is that (80 ± 20)% of the uranium associates with organic matter and any uranium which does not so associate may with almost equal confidence be associated with pyrite or with

* Columbia University Mineral Beneficiation Laboratory. Including work by M. D. Hassialis, J. Killelea, N. Levine, and R. C. Musa.

Table I. Typical Mineralogical Composition of Chattanooga Shale

Quartz + feldspar	58.38%
Clay	11.44%
Pyrite	8.14%
Carbon	9.62%
Hydrogen	1.03%
Organic sulfur	2.19%
Fe_2O_3	3.19%
Al_2O_3	3.29%

the silicates-clays or with both. In a concurrent study Bates[3] reports a correlation coefficient of 0.698 for U vs C and a coefficient of +0.567 for U vs pyrite and negative correlation coefficients of −0.809, −0.70 and −0.763 for U vs clay, quartz and Fe_2O_3 respectively.

Similar techniques were used to associate the uranium which is more refractory to leaching with various components of the ore. Table III gives a comparison between uranium extracted at a variety of acid concentrations together with the relative X-ray line intensities for clay and pyrite determined on the residue from a raw-shale leach. Leaching was performed at 90–100°C on −400 mesh shale for a period of 2 hr. Although there does exist a concomitant increase with uranium extraction with clay transformation, a statistical check of the hypothesis that the refractory uranium is associated with the clay leads to a negative conclusion. The increase of uranium extraction with pyrite transformation is less apparent and is, in fact, equally denied by statistical calculation.

Table II. Assays of Infrasizer Fractions of a Micronized Raw Shale

Sample no.	*Uranium, %*	*Pyrite, %*	*Carbon, %*
A44-1	0.0084	11.6	14.09
A44-2	0.0090	13.4	14.25
A44-3	0.0093	14.2	14.74
A44-4	0.0083	14.2	13.49
A44-5	0.0064	10.6	9.89
A44-6	0.0065	10.3	10.08
A44-7	0.0074	13.2	11.74
A44-8	0.0098	16.9	11.67
A44-9-1	0.0084	10.5	14.38
A44-9-2	0.0100	11.7	14.61
A44-9-3	0.0093	13.0	14.04
A44-9-4	0.0088	13.6	14.68
A44-9-5	0.0074	10.1	12.51
A44-9-6	0.0083	11.7	13.01
A44-9-7	0.0091	10.4	15.20
A44-9-8	0.0104	7.4	17.31
44-9-1	0.0078	10.8	13.36
44-9-2	0.0085	12.8	14.03
44-9-3	0.0085	13.2	14.15
44-9-4	0.0080	12.5	11.71
44-9-5	0.0071	11.0	11.29
44-9-7	0.0085	10.4	13.11
44-9-8	0.0099	7.3	14.53
44-1	0.0082	10.6	13.29
44-2	0.0087	11.6	13.42
44-3	0.0082	13.5	13.21
44-4	0.0078	12.1	11.48
44-5	0.0067	11.4	9.99
44-7	0.0073	11.7	11.51
Mean	0.00834	11.87	13.13

Leaching as a method of beneficiation owes its importance to its ability to select values on a molecular scale, hence its increasing utility in the recovery of complex, finely-disseminated values. It is a function of a large number of operational variables which may be divided roughly into physical and chemical factors. Whereas the chemical factors suffer little change as the grade of the ore decreases, the relative importance of the physical factors changes drastically often to the point of becoming controlling.

Successful leaching of the values from an ore is based upon satisfaction of the following criteria: (1) The values to be leached must be exposed. (2) The exposed sites of the values must be accessible to the leaching agent. (3) The values or a reaction product of the values and a component of the leach solution must be soluble in the leach liquor. (4) Practical transport of the values from the exposed site to the main body of the leach liquor must take place.

Exposure of the values is usually achieved by breakage or by chemical or thermal removal of a portion of the protective shell. Exposure does not mean liberation of values as in flotation, it means only the existence of an opening to the outside. Thus a mass of value completely enclosed within a leaching-agent-impermeable shell is neither exposed nor liberated. If, however, a small adit exists connecting this mass of value to the outside and through which leaching liquor may move, the value is exposed though not liberated. When transport of values and leaching solution through this adit is so slow that only negligible amounts of the values can be moved to the outside in reasonable time, the exposure is not practical and the values may be said to be unexposed.

Accessibility of the values does not automatically follow their exposure. Thus, in the example used above, if the adit is entered by a leaching solution which makes a contact angle of more than 90 degrees with the walls of the adit, movement of the leaching solution into the adit will cease. Accessibility may be achieved under those circumstances by increasing pressure or by changing the contact angle by means of a suitable surface-active agent.

Once the leaching solution reaches the exposed site, it must be able to dissolve the values directly or first react with them to produce a soluble product;

Table III. Uranium Extraction vs Clay and Pyrite Remaining in the Residue

		Relative line intensities	
Conc. H_2SO_4 % by wt	*% U extracted*	*Clay d = 9.98–10.14*	*Pyrite d = 2.715 2.718*
0	10.0	23.6	6.3
5	73.3	34.5	9.1
15	81.0	30.0	8.3
25	83.3	21.2	9.7
35	84.0	22.5	8.3
50	84.7	9.9	6.6
65	92.7	5.8	7.4
75	94.0	0.0	8.1
90	94.0	0.0	1.8

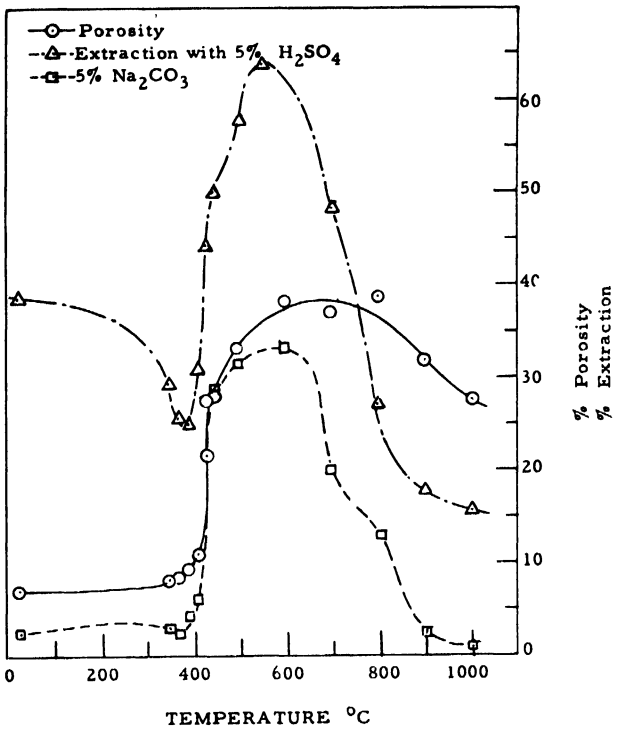

Figure 1. Uranium recovery with H_2SO_4 and Na_2CO_3 and porosity vs temperature of roast

in this manner immobile values are given mobility. This vital element of leaching is primarily chemical in nature.

The values now mobilized by dissolution must move out through the adit to join the main body of the leaching solution. This transportation of values may take place convectively or diffusionally. In general, transport from sites exposed at the surface of a particle may be made convective by agitation; however transport from interior-surface sites is usually diffusional.

It should be noted that all of these criteria, except the third, are of a physical nature. The problem of finding suitable parameters to characterize the physical aspects of the leaching problem has not received the attention it merits. With reference to shale, an exploratory program was based on determination of pore-size distribution[5] arbitrarily divided into macro- and microporosity, specific surface,[6,7] permeability,[8] and diffusivity. It was recognized that these parameters were not truly independent but it was not initially possible to select between them on the basis of the original model assumed for the ore. This model envisaged very fine inorganic particles of quartz pyrite, illite, feldspar, chlorite, marcasite and of accessory minerals embedded in a continuous matrix of an organic material called kerogen, the inorganic particle being arranged in strata. The uranium was assumed to be dispersed in the organic phase or at the organic-inorganic interfaces. It was assumed that pyrolysis of kerogen followed by evaporation of the volatile decomposition products would not result in loss of uranium. Thus thermal treatment of the shale should expose the uranium which should transfer from the decomposed, volatilized and oxidized kerogen to the surface of the inorganic minerals.

Samples were thermally treated at a variety of conditions, their physical parameters determined and their leachability measured by means of 5% H_2SO_4. Figure 1 shows the porosity developed and the extraction achieved for a variety of ½ hr thermal treatments, while Fig. 2 shows macro- and microporosity achieved for 72-hr roasts. It should be noted that total porosity is predominantly macroporosity. For most temperatures below 390° C no correlation is apparent between extraction and any porosity. From 390°C to about 550°C the correlation between extraction and macro- or total porosity is excellent and is independent of chemical nature of the leaching agent. It should also be noted that the correlation between extraction and macroporosity shown in Fig. 2 for a 72-hour roast is equally good though the chemical nature of the two roasted materials differs. As may be seen from Fig. 3, S and C are eliminated at 450–500°C and 320°C respectively, hence shorter roast times give products containing more C and S. In spite of this different chemical environment, the correlation persists. Note also that the development of macroporosity is coincident with carbon and sulfur removal.

Microporosity and specific surface are not too surprisingly correlated as may be seen in Fig. 4. Further X-ray data show that microporosity develops as pyrite is converted to what is probably a spongy iron oxide. The peak in microporosity at 550°C corresponds to an unexplained peak exhibited by differential thermal analysis. Subsequent loss in microporosity is associated with sintering effects. In

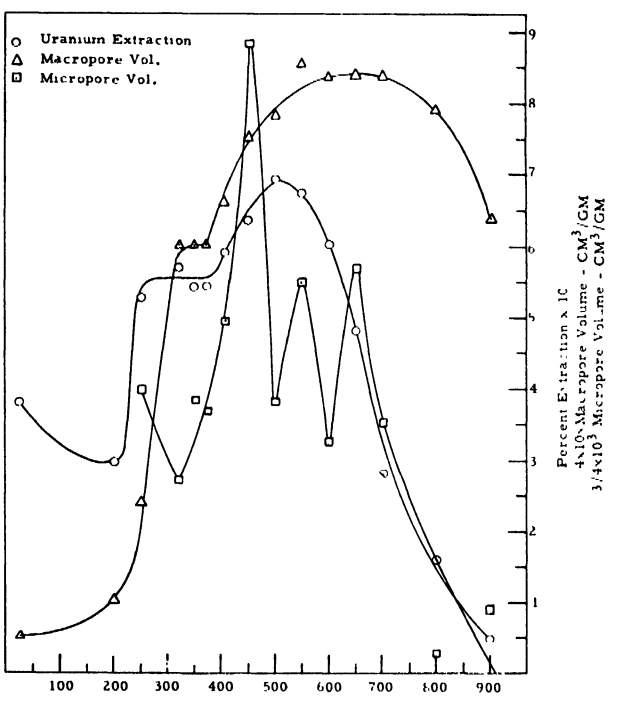

Figure 2. Micro- and macroporosity and recovery vs roasting temperature

the region above 650°C extraction correlates with microporosity. This and other evidence not herein presented points strongly to the conclusion that for constant chemistry the exposure of uranium sites and the transport out of pores controls recovery. Conversely, for constant physical character the chemical nature of the leaching agents controls.

The unusual features of the problem of recovering uranium from leach solutions derived from low-grade ores stem from the fact that the applicable methods must be made to work at the extreme low end of the range of utility. All leaching operations result in a dilution of uranium owing to a change in density and volume of the carrier. The main factors are the ratio of weight of leaching solution per unit weight of ore (which is normally the pulp density) and the ratio of weight of washing solution per unit weight of ore. The sum of these two ratios is the over-all dilution factor, which may be as low as 1 or as high as 7 with 3 a not improbable average. Thus, an ore assaying 0.01% or 100 ppm of uranium which is leached with a 92% recovery at an over-all dilution factor of 4 will give a leach solution containing $100 \times 0.9/4 = 23$ ppm. An ore assaying 0.1% will give under similar conditions a leaching solution containing 230 ppm. It is apparent that for equal recovery and dilutions the grade of ore controls the concentration of the leaching solution.

Virtually all solution processing is currently being accomplished by ion-exchange resins. Figure 5 shows an estimate of the cost of processing solutions of varying uranium content. The estimate is based on a plant processing 500,000 lb of uranium per year

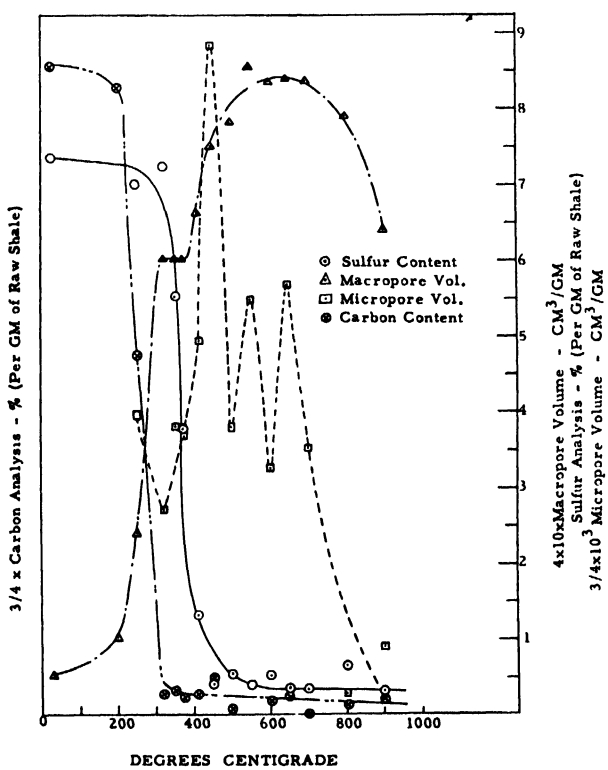

Figure 3. Sulphur and carbon content vs roasting temperature

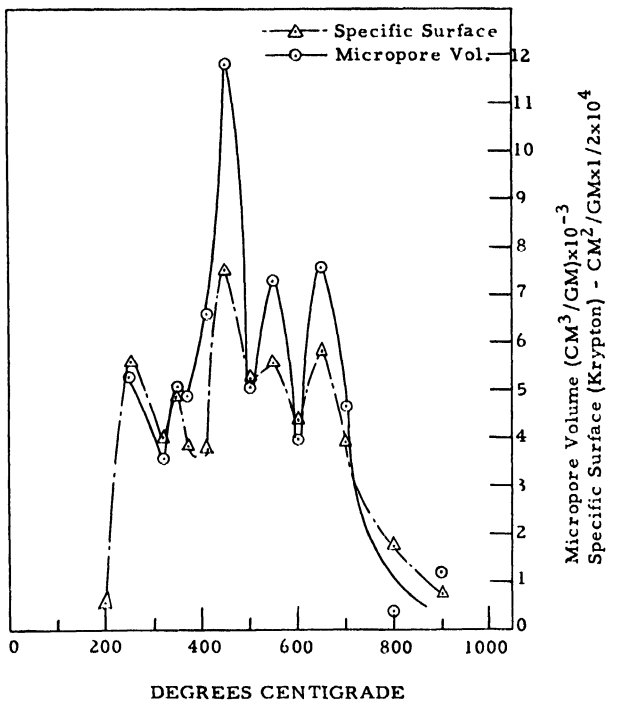

Figure 4. Microporosity and specific surface vs roasting temperature

from a clarified leach solution; a 10-year resin life being assumed. Resin "poisoners" present in the solution will, by shortening resin life, increase costs. Since resin capacity falls off sharply with decreasing pH below a pH = 1.4 costs will increase exponentially. Note the sharp rise in costs of ion-exchange at solution concentrations below 50 ppm.

The most desirable method of using ion-exchange is by putting the resin in the pulp. This eliminates the need for residue washing so that a lower dilution factor is used and it avoids filtration. For these reasons, although there are greater resin losses and resin handling costs, there is an over-all economy.

The use of a continuous ion-exchanger offers the attractive feature of a saving in resin inventory by a factor of 4. Counterbalancing is the need to separate sands from slimes and the additional grinding cost which may be carried to reduce all the ore to a suitable size. No decision on principle is apparent, rather each case will have to be judged individually.

The steep rise in costs for ion-exchanging of clarified solutions containing less than 50 ppm uranium, may be expected to hold also for the other ion-exchange techniques. It is due to a drop in uranium capacity of the resin with decreasing concentration. The use of a cascade resin-in-pulp system or of cascade leaching of slimes in conjunction with a continuous exchanger may serve to shift the onset of the steep rise in cost towards lower concentrations.

Another method of recovering uranium from leach liquors is liquid-liquid solvent extraction. Its cost is comparable to the cost of ion-exchanging clarified solutions but not to resin-in-pulp and continuous ion-exchanging techniques. If, however, a pH below

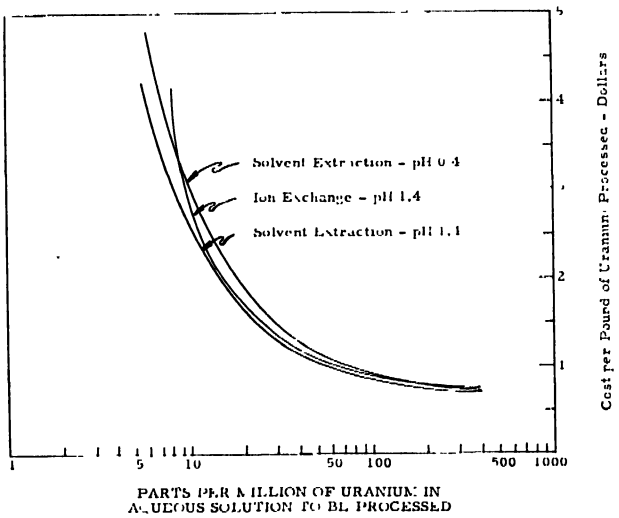

Figure 5. Estimated cost of processing clarified solutions for uranium. Basis is 500,000 pounds annual uranium production

1.0 must be maintained, then, since the extractants tend to retain their effectiveness while resins lose theirs, solvent extraction becomes very attractive—particularly since there are some indications that solvent extraction may be used with slimes without excessive emulsification or reagent loss due to chemisorption or reaction with the ore.

The factors which affect economy and which stem from the fact that the grade of the leach solution is very low are:

Entrainment losses, i.e., loss of organic phase to aqueous phase by dispersion of the former in the latter. This is dependent upon extraction equipment, volume of aqueous throughput and on the presence of chemicals or colloidal solids capable of stabilizing the dispersion. Hence, decreasing uranium concentration with its reciprocal increase of volume of aqueous phase per unit weight of uranium recovered leads to an increase in entrainment loss per unit weight of uranium. Hence if the cost of extractant due to entrainment loss per unit weight of uranium is to be kept constant, the entrainment loss per volume of solution treated must be decreased in proportion to the decrease in concentration.

Solubility losses, i.e., losses of organic diluent or of extractant to the aqueous phase are directly proportional to the volume of aqueous throughput. Hence, solubility losses increase as concentration decreases. So, to keep the cost of solubility losses per unit weight of recovered uranium constant, the solubility losses per unit volume of aqueous phase must be decreased in proportion to the decrease in uranium concentration. If the extractant is more costly than the diluent (which it usually is) then an increase in the distribution coefficient will permit a decrease in ratio of extractant to diluent, hence, for equal entrainment loss of these solvents a saving in cost is effected.

Stripping reagent costs per unit weight of uranium processed and regeneration reagent cost, where necessary, vary inversely with the uranium concentration in the extract solution. At low uranium levels, the equilibrium distribution coefficient, uranium concentration in organic phase per unit uranium concentration in aqueous phase, is essentially independent of concentration so that reagent costs per unit weight of uranium processed vary inversely with the product uranium concentration in the aqueous phase multiplied by the distribution coefficient.

Entrainment loss is a problem of equipment and its operation. In order to cut down contact time, good contacting of the two phases is required. This is usually produced by turbulence, a condition which normally aggravates entrainment and emulsification. Development of more insoluble solvents and extractants will reduce solubility losses. Development of a high distribution-coefficient extractant (which normally implies good selectivity for uranium) will reduce stripping and regeneration plant size and cost. Of all the factors the most critical for the extraction from low-grade solutions are entrainment and solubility losses.

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Alkaline Leaching of Uranium Ores

By F. M. Stephens, Jr. and R. D. Macdonald,* USA

SUMMARY

To be soluble in carbonate solutions, uranium must be in the hexavalent (uranyl) state. If it exists in the plus 4 state, it first must be oxidized, preferably by the oxygen in air at temperatures in excess of 71°C (160°F).

There are three modifications of the current commercial carbonate leaching practice.

1. The salt-roast carbonate leach, in which high-vanadium carnotite-type ores are roasted with sodium chloride and then leached with carbonate solutions. This type of plant is typified by the Monticello, Utah, plant of the US AEC.

2. A raw-ore leach, in which oxidized ores are leached in sodium carbonate-bicarbonate solution at substantially atmospheric pressure. This type of plant is typified by the Grants, New Mexico, plant of the Anaconda Copper Mining Company.

3. A raw-ore leach, in which partly oxidized or primary ores (pitchblende, uraninite) are leached in sodium carbonate-bicarbonate solutions at elevated temperatures in the presence of an oxidizing agent such as potassium permanganate or air. This method is typified by the Beaverlodge, Saskatchewan, Hydrometallurgical Plant of Eldorado Mining and Refining Limited.

Simplified flowsheets of these plants are presented.

INTRODUCTION

In the chemical processing of low-grade uranium ores, either acids or carbonate reagents may be used as lixiviants for dissolving the uranium. This paper discusses the carbonate leaching methods most commonly used and gives examples of operating mills that use each of the three modifications of the carbonate leaching flowsheet.

Before describing the details of the carbonate methods, the principal reasons for using such a system should be considered. For example, the alkaline leach has found favor because the corrosion problems in such a system are negligible as compared with those encountered in acid circuits. In most variations of the process, the bulk of the reagents used for leaching can be reclaimed and returned to the plant. For uranium-bearing limestones and other high lime (CaO) ores, acid consumption would be prohibitive and a carbonate circuit must be used. Carbonate leaches are almost specific for uranium and vanadium, a fact which simplifies recovery of the values from solution. Sodium carbonate is a relatively cheap reagent and offers few, if any, disposal problems.

In spite of these advantages, carbonate is not ideal in many respects. Among its disadvantages is the fact that it is seldom possible to get extractions quite so good as those obtained with acid. It is not suitable for ores high in gypsum or sulfides. Thickening and filtering (in the absence of flocculents) are difficult operations with carbonate solutions, and there are numerous refractory uranium minerals such as euxenite, betafite, samarskite, brannerite, and davidite which are not attacked significantly by carbonate solutions without a prior fusion step.

In North America, the carbonate leaching system is being used in three modified forms, all of which use mixtures of sodium carbonate and sodium bicarbonate in aqueous solution as leaching agents. These three modifications are:

1. The salt-roast carbonate leach process, in which high-vanadium carnotite-type ores are first roasted with sodium chloride and then leached in sodium carbonate solutions.

2. A raw-ore leach, in which highly oxidized ores are leached in sodium carbonate-sodium bicarbonate solutions at atmospheric pressure.

3. A raw-ore leach method, in which unoxidized or primary ores are leached in sodium carbonate-sodium bicarbonate solutions at elevated temperatures in the presence of an oxidizing agent such as potassium permanganate or air.

CHEMISTRY OF CARBONATE LEACHING

In all three principal modifications of the carbonate leaching process, the uranium eventually goes into solution as sodium uranyl tricarbonate, $Na_4UO_2(CO_3)_3$. However, in each system, the chemical reactions involved in reaching this endpoint differ. The principal chemical reactions involved in salt roasting, leaching, precipitation, and reagent regeneration are discussed in the following sections of this paper.

Salt Roasting

The salt roasting process[1] was devised as a method for extracting vanadium from oxidized carnotite ores and, as a result, much of its chemistry is as much concerned with vanadium recovery as with uranium. Salt roasting does not improve the extraction of uranium from carnotite ores over that which

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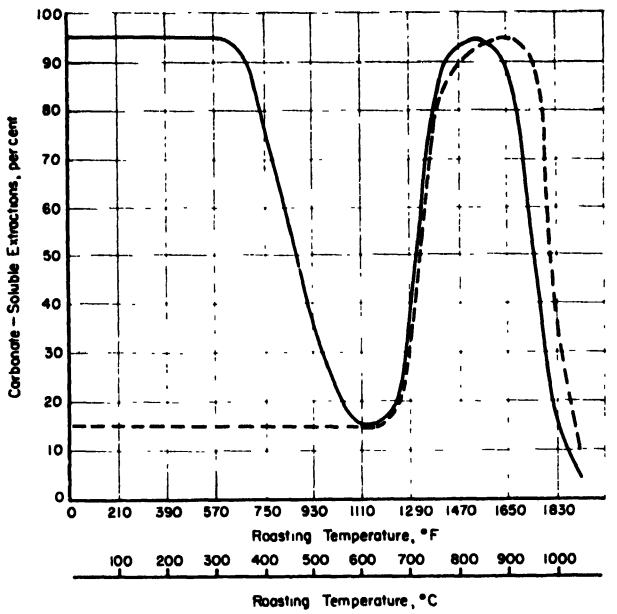

Figure 1. Effect of salt-roasting temperature on extraction of uranium and vanadium in sodium carbonate-sodium bicarbonate solutions

can be obtained from a sodium carbonate-sodium bicarbonate leach of the unroasted ore (Fig. 1), but it improves vanadium extraction materially. In fact, poor temperature control during roasting may result in uranium extractions which are inferior to those obtainable in leaching the unroasted ore. This situation results from the fact that in salt roasting, four distinct physical or chemical changes occur as a function of temperature. For example, with carnotite these are:

1. Temperature range to 350°C (662°F). The mineral carnotite is stable and remains soluble in Na_2CO_3–$NaHCO_3$ solutions.

2. Temperature range of 350°C (662°F) to 600°C (1112°F). The mineral carnotite loses its water of hydration and/or decomposes to form a uranium complex which is insoluble in Na_2CO_3–$NaHCO_3$ solutions.

3. Temperature range of 600°C (1112°F) to 850°C (1562°). Sodium chloride reacts with vanadium minerals to form sodium vanadates. Sodium vanadates react with uranium compounds to form sodium uranyl vanadates which are soluble in Na_2CO_3–$NaHCO_3$ solutions.

4. Temperature range of 850°C (1562°F) to 1000°C (1832°F). Sodium uranyl vanadates and sodium vanadates decompose or react with silica to form silicates which are insoluble in Na_2CO_3–$NaHCO_3$ solutions.

Because reaction 3 is reversible, it is necessary to quench the roasted ore as rapidly as possible after roasting to prevent the sodium uranyl vanadate from reverting to a sodium vanadate and an insoluble uranium complex. Similar reactions occur with other uranium minerals and compounds.

The actual soluble uranium compound formed in the salt-roasting step is a complex vanadate; so salt roasting is not a feasible method for converting uranium minerals to the carbonate-soluble form unless sufficient vanadium is present in the ore to form the sodium uranyl vanadate.

In salt roasting ores high in calcium carbonate, there is a tendency for calcium uranates to form in preference to sodium uranyl vanadates. Because the calcium uranates which form are not soluble in Na_2CO_3–$NaHCO_3$ solutions, it is not possible to extract uranium efficiently from high-lime ores after a normal salt roast. This difficulty can be overcome in part by the artificial addition of a sufficient amount of excess vanadium in the form of V_2O_5 to react with the calcium carbonate to form soda-soluble calcium vanadate in preference to insoluble calcium uranates.

Leaching

In natural ores or in roasted products, uranium usually is found in either the quadrivalent (uranous) or the hexavalent (uranyl) state. To dissolve in carbonate solution, that is, to be capable of forming the uranyl tricarbonate complex anion, the uranous form must be oxidized to the uranyl form. This oxidation can be accomplished with the oxygen of the air during dry roasting or by bubbling air through an aqueous suspension of ground ore. The rate of oxidation is great enough to be useful at temperatures in excess of about 71°C (160°F). Potassium permanganate is an effective, though somewhat expensive, oxidant.

In the oxidized uranium minerals—such as carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$; tyuyamunite, $CaO \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$; autunite, $CaO \cdot UO_3 P_2O_5 \cdot nH_2O$; uranophane, $CaO \cdot 2UO_3 \cdot 2SiO_2 \cdot 6H_2O$; torbernite, $CuO \cdot 2UO_3 \cdot P_2O_5 \cdot 12H_2O$; soddyite, $5UO_3 \cdot 2SiO_2 \cdot 6H_2O$—the uranium is present in the hexavalent state. Its dissolution can be expressed as:

$$UO_3 + 3CO_3^{--} + 2H_2O \rightarrow UO_2(CO_3)_3^{4-} + 2OH^- \quad (1)$$

In primary uranium minerals — such as pitchblende, $nUO_2 \times UO_3$ amorphous; and uraninite, $nUO_2 \times UO_3$ crystalline, or in partly oxidized minerals such as gummite, $U_3O_8 + PbO$ + others, variable part of the uranium is present as uranous and part as uranyl. The dissolution of the uranous portion can be expressed as:

$$UO_2 + \tfrac{1}{2}O_2 + 3CO_3^{-} + H_2O \rightarrow UO_2(CO_3)_3^{4-} + 2OH^- \quad (2)$$

Both of these dissolution reactions produce hydroxyl ion and both are reversible. For optimum results, the hydroxyl ion must be removed as it is formed, which is usually and preferably done by neutralizing it with bicarbonate ion, thus:

$$HCO_3^- + OH^- \rightarrow CO_3^{--} + H_2O \quad (3)$$

tending to drive Reactions 1 and 2 toward completion to the right. This simple explanation probably

is not the complete story because experimental evidence and data from operating plants show that best results are obtained if the bicarbonate ion concentration is manifold greater than that required for stoichiometric neutralization of the hydroxyl ion formed.

Sulfide minerals in the ore, commonly pyrite, consume soda ash to produce sodium sulfate and, simultaneously, bicarbonate:

$$2FeS_2 + 8Na_2CO_3 + 7\tfrac{1}{2}\,O_2 + 7H_2O \rightarrow 2Fe(OH)_3 + 4Na_2SO_4 + 8NaHCO_3 \quad (4)$$

Within limits, this can be a beneficial reaction because of the bicarbonate produced, but if there is more than about one per cent of pyrite in the ore, the sodium sulfate produced is more than conveniently can be bled from the circuit as a normal soluble loss, so a deliberate sulfate bleed must be included. This bleed is commonly in the form of a discarded barren solution, but it represents a substantial loss of relatively expensive sodium ion. Sodium sulfate within reasonable concentrations does not seem to have a deleterious effect on carbonate leaching. Successful commercial cyclic leaches have been run with as much as 175 grams of sodium sulfate per liter present in the carbonate leach liquor.

If the ore to be leached contains gypsum or magnesium sulfate, these too will react to produce sodium sulfate with an eventual resultant reagent loss.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4 \quad (5)$$

Precipitation

Normally uranium is precipitated by the addition of sodium hydroxide. This can be done because Equations 1 and 2 are essentially reversible. If the hydroxyl ion concentration becomes great enough, sodium diuranate will precipitate.

$$2UO_2(CO_3)_3^{4-} + 6OH^- + 2Na^+ \rightarrow Na_2U_2O_7\downarrow + 6CO_3^{--} + 3H_2O \quad (6)$$

In initiating precipitation by the addition of sodium hydroxide, bicarbonate ion is first destroyed.

$$HCO_3^- + OH^- \rightarrow CO_3^{--} + H_2O \quad (3)$$

Sodium hydroxide will precipitate the uranium in the range of about pH 11. If precipitation is done in the cold, it will be more complete than if done hot, but the precipitate will be so finely crystalline and difficult to filter that hot precipitation is preferred. Laboratory work indicates that some of the newer flocculents may be useful for cold precipitation. Incomplete precipitation is not considered serious because the "barren" solution normally is re-used in leaching. However, if there is a necessary solution bleed in order to keep a solution balance, quantitative precipitation of uranium is a necessity. An excess of sodium hydroxide of about five grams per liter will produce a satisfactory precipitation rate and a filterable precipitate.

An alternative way of precipitating uranium involves destroying the carbonate ion by the addition of sulfuric acid to pH 3, boiling or evacuating to remove all carbon dioxide, and then adding ammonia or caustic soda to pH 7 to precipitate uranium as the hydroxide or uranate. This method, though effective, has not found favor because it requires destruction of the expensive leaching reagent.

If the vanadium present is at least stoichiometric to the uranium ($2U:V_2O_5$), extremely complete precipitation can be effected from carbonate solution merely by adding acid to neutrality to form an artificial carnotite, the "yellow cake" often used in Colorado plateau metallurgy. The reaction is complex but may be represented approximately by the following:

$$Na_4UO_2(CO_3)_3 + \begin{Bmatrix} Na_2V_2O_7 \\ NaVO_3 \\ Na_3VO_4 \end{Bmatrix} + 6H_2SO_4 \rightarrow Na\cdot UO_2\cdot VO_4\cdot nH_2O\downarrow + 6NaSO_4 + 3CO_2\uparrow + 3H_2O \quad (7)$$

"Yellow cake" is relatively easy to filter, but it requires a further fusion and water leach to separate the vanadium from the uranium. Use of the "yellow cake" method depends on the value of vanadium. If vanadium is present and is desired, then the method is useful, but if vanadium is not to be recovered, then an alternative method for uranium precipitation is to be preferred.

After the precipitation of "yellow cake," the solution often contains additional vanadium. This can be recovered as "red cake," or V_2O_5, by further proceeding with the acidification after the "yellow cake" is filtered off.

Forward and Halpern[2,3,4] have reported laboratory data which show that in an autoclave at temperatures of the order of 100–150°C (212–302°F), gaseous hydrogen will reduce the uranium in the uranyl carbonate complex and black oxide (UO_2) will precipitate. This reaction, which must be catalyzed to have a useful rate (the authors prefer to use metallic nickel powder), takes a very short time, produces a high-grade final product, and the barren solutions are suitable for re-use. The reagent consumption is small, but the uranium product must be subjected to magnetic separation to recover the nickel catalyst for re-use. There are no commercial applications of this method as yet, perhaps because the simplicity of the more or less standard diuranate precipitation has made it difficult to justify the development expense required to put the hydrogen reduction method to commercial use.

Reagent Regeneration

One of the advantages of carbonate leaching is that the leaching reagents can be regenerated simply and economically. The precipitation process does part of the regeneration.

$$Na_4UO_2(CO_3)_3 + 4NaOH \rightarrow Na_2UO_4 + 3Na_2CO_3 + 2H_2O \quad (8)$$

The excess sodium hydroxide necessary for precipitation (5 to 10 grams per liter) can be con-

verted to sodium carbonate and the bicarbonate concentration can be increased again by passing carbon dioxide through the barren carbonate solution.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad (9)$$

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \quad (10)$$

This procedure is particularly attractive because most plants have a supply of waste CO_2 available in the form of flue gas from a steam boiler or, if the ore is roasted, in the waste roaster gas. Thus, the reagent regeneration is accomplished inexpensively.

Carbonation can be obtained satisfactorily in a standard packed tower with solution descending through the packing while CO_2-rich gas passes upward. For very hot or dirty gas, it may be desirable to use a scrubber-packed tower system in which the CO_2-rich gas is cooled and scrubbed in a spray tower containing horizontal baffle plates, before passing to the bottom of the packed tower.

This system has been shown in practice to produce satisfactory concentration of bicarbonate.

FACTORS AFFECTING REACTION RATES

Temperature

For over thirty years, the carbonate leaching plants of the Colorado plateau area have operated with hot solutions. It has been recognized that the rate of uranium dissolution is improved as the temperature rises and furthermore, that extractions are consistently higher with hot solutions. The best published data on this subject are in the recent articles of Forward and Halpern,[2,4] which show that at 100°C (212°F) the extraction of uranium in three hours is nearly twice as great as at 60°C (140°F). Furthermore at temperatures above boiling, up to 115°C (239°F), this rate increase continues.

A commercial outgrowth of the work of Forward and Halpern is the Beaverlodge refinery of Eldorado Mining and Refining Limited[5]. Here, pitchblende ore is leached in carbonate-bicarbonate solution at a temperature of 104°C (220°F) and about 80 psig. Compressed air introduced into the agitated leaching autoclaves serves as the oxidant, with satisfactory extraction being obtained in about 16 hours of retention time.

From the recorded data[2,4,5] it appears that rapid oxidation of primary uranium (pitchblende uraninite) is obtained at temperatures in excess of 100°C (212°F) and useful rates are obtained as low as 71°C (160°F).

Oxygen Concentration

Although the rate of leaching is greater in hot than in cold solutions the solubility of oxygen in carbonate solutions decreases as the temperature increases. Where it is necessary to maintain oxidizing conditions in uranium leaching systems, this decreased solubility can be compensated for by increased pressure or by rapid agitation to give a mechanical mixture of air and pulp.

At temperatures approaching boiling, the oxygen in air will oxidize uranous uranium to uranyl at a reasonable rate,[4] but if the air is enriched in oxygen or the partial pressure of oxygen increased by increasing the total air pressure, the rate of oxidation increases rapidly. In practice, it is necessary to balance the value of increased rate of oxidation with the cost of maintaining an increased oxygen partial pressure.

It seems clear that, unless the ore to be treated is completely oxidized in nature, or is to be given an oxidizing roast, oxidation is an essential part of any carbonate leaching step, whether it be done in an autoclave at more than atmospheric pressure or in an open leaching vessel for an extended leaching time.

Reagent Concentration

Although the solubility of $Na_4UO_2(CO_3)_3$ is reputed to be greater in water than in either carbonate or bicarbonate solutions, in actual practice carbonate-bicarbonate leaching solutions carry from 5 to 10 per cent of sodium carbonate and from 1 to 7 per cent of sodium bicarbonate. Most operators believe that better results can be obtained with carbonate-bicarbonate mixtures than with either reagent alone. There is laboratory evidence, however, that satisfactory extractions can be obtained with bicarbonate solutions alone. Perhaps some of the difference of opinion in this matter can be ascribed to the difficulty of obtaining reliable and precise determinations of carbonate and bicarbonate contents. Most such determinations in plants are the result of crude potentiometric titrations and are at best only an indication of the true solution composition. A further beclouding factor is the impurity of reagents. Much that is sold as pure sodium carbonate or bicarbonate is a mixture of the two, or of the two and other salts.

The practice of carbonate leaching of uranium shows that high reagent concentrations can be correlated with high uranium extractions. There is a practical limit, however, because the higher the reagent concentration, the more soluble loss of reagent in the leached residue (tailings).

Particle Size

As in all leaching operations, the specific surface available must control the rate of chemical reaction, so the finer the grind, the faster and more complete will be the leach. But in practice, it is found for the carbonate leaching of most ores that a grind to essentially minus 100 mesh is fine enough and that finer grinding does little good. This is particularly true of sandstone ores where the uranium is in the cementing material which bonds the 65 to 100 mesh silica sand grains.

For the carbonate leaching of certain refractory uranium compounds, it has been reported beneficial to grind to nominally minus 325 mesh.

Agitation

In any leaching reaction where gas-liquid or gas-solid contact is controlling, good agitation is essential

for optimum results. This can be obtained in an open agitator, in agitated autoclaves as at Anaconda's Grants, New Mexico, plant,[6] in horizontal agitated autoclaves as at Beaverlodge,[5] or probably even in air-agitated Pachuca tanks. Whatever the type of leaching vessel, it is preferred for reasons of ease of suspension to work with as high a pulp density as possible, preferably in the range of 50 to 60 per cent of solids and with at least three leaching vessels in series, to prevent short circuiting.

If there were any practical means to dispense air in a pulp in micron-sized bubbles, it might improve reactions involving oxidation. But most attempts to accomplish this, as by the use of frits or punched rubber sheets, have failed because of rapid plugging of small holes with precipitated salts such as gypsum. In a recent installation, expendable glass cloth is employed as the frit and is reported to be successful.

Possible Improvements in Carbonate Leaching

Unless an ore contains refractory uranium minerals such as euxenite or samarskite,[7] or a high-sulfide or sulfate gangue, carbonate leaching usually can extract in excess of 90 per cent of the uranium content. But this is normally slightly less than can be obtained by acid leaching and sometimes significantly less. Furthermore, the reagent losses in carbonate leaching are relatively high.

For the future, we must be concerned with ways to avoid wasting some of the uranium, which now leaves the processing plants with the tailings. One possible helpful step is to replace the difficult, expensive, and sometimes inefficient filtration step with a countercurrent decantation system. Until 1954, this was not a reasonable possibility in most plants because of the poor setting characteristics of most carbonate-leached pulps. But with the advent of the new flocculating reagents such as Aerofloc–3000 (American Cyanamid Company) and Separan–2610 (Dow Chemical Company), multi-step countercurrent decantation looks attractive as a means of reducing soluble losses.

A further increase in extraction probably will come from the use of more rigorous leaching conditions: longer time, higher temperature, greater oxygen partial pressure, finer particle size, and better dispersion of air. With all the recent intensive work on carbonate leaching, no one to our knowledge has investigated adequately the effect of leaching temperatures above 150°C (302°F).

Examples of Three Types of Carbonate Plants

In order to understand more fully the actual use of the three modifications of carbonate leaching processes now in operation, plant flowsheets of a salt-roasting plant for the treatment of high-vanadium ores at Monticello, Utah, a raw-ore leaching plant for the treatment of oxidized uranium ores at Grants, New Mexico, and a raw-ore leaching plant for unoxidized or primary uranium ores at Beaverlodge, Saskatchewan, are given in the following sections of this paper.

Flowsheet of Salt-Roasting Mill of US AEC at Monticello, Utah[8]

In the Monticello Mill, after a conventional dry-crushing and sampling operation, the ore follows the flowsheet shown in Fig. 2. The ore is stored in fine ore bins which feed the roasting and leaching section of the mill. The ore coming from these bins is weighed, sampled, and fed by a bucket elevator to the top hearth of an 18-foot-diameter 8-hearth roaster. The returning fines from the dust-collection system and 6 to 9 per cent sodium chloride are mixed with the feed going to the roaster. The roaster is operated at a maximum temperature of 850°C (1562°F).

As it leaves the roaster, the ore is quenched in a stream of 3 per cent sodium carbonate solution, and the resulting slurry is given a light grind in a ball mill to free the natural sand grains from their cementing material. The ball mill operates in closed circuit with a spiral classifier. The classifier overflow goes to three agitators operating in series at a temperature of 92 to 96°C (198 to 205°F).

Following agitation, the slurry undergoes a liquid-solid separation step involving a four-stage countercurrent decantation in thickeners followed by a final filtration step on the solids. The pregnant liquor goes to clarification and precipitation. In the precipitation step, the uranium is precipitated as "yellow cake" (artificial carnotite) by adjusting the pH of the solution to 6 with sulfuric acid. The "yellow cake" is then filtered out in plate-and-frame presses and is further refined by fusion with sodium carbonate, salt, and sawdust to form water-soluble vanadium which is removed by leaching.

The uranium-free liquor is treated for vanadium recovery by again adjusting the pH with sulfuric acid to a value of 2.5, at which point the vanadium precipitates as "red cake" which is filtered out and fused to give a final product of black V_2O_5.

Flowsheet for the Leaching of Unroasted Oxidized Uranium Ores at the Grants, New Mexico, Plant of the Anaconda Copper Mining Company[6, 9]

The flowsheet for the leaching and precipitation sections of the Grants, New Mexico Mill is shown in Fig. 3. In the flowsheet, which follows a normal crushing and sampling plant, the fine ore is fed from storage bins, by means of feeders which also serve as weighing devices, directly by belt conveyor to a rod mill operating in open circuit. The rod-mill discharge is fed to the ball-mill circuit, where the ball mill operates in closed circuit with a wet cyclone acting as a classifier. All grinding is done in carbonate solutions.

The ground ore is next charged to batch-operated autoclaves where it is leached at 60 per cent of solids and a temperature of 107–121°C (225 to 250°F) and a pressure of 15 psig for approximately 6 hours in a solution containing 10 per cent sodium carbonate and 1 per cent sodium bicarbonate. After leaching, the slurry is filtered and washed in Burt pressure filters. The pregnant solution then is sent

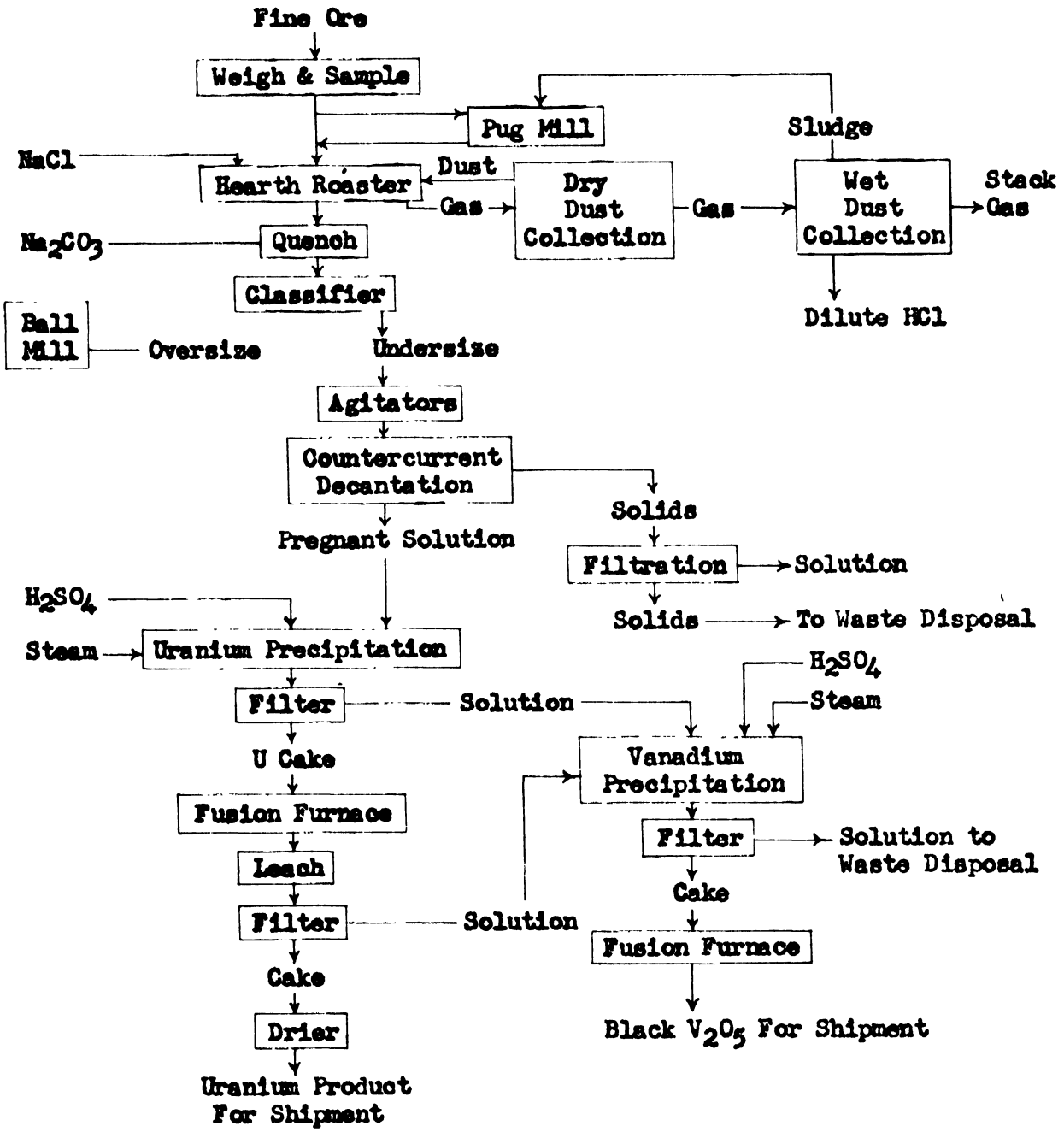

Figure 2. Flowsheet of the salt-roasting mill of the US AEC at Monticello, Utah

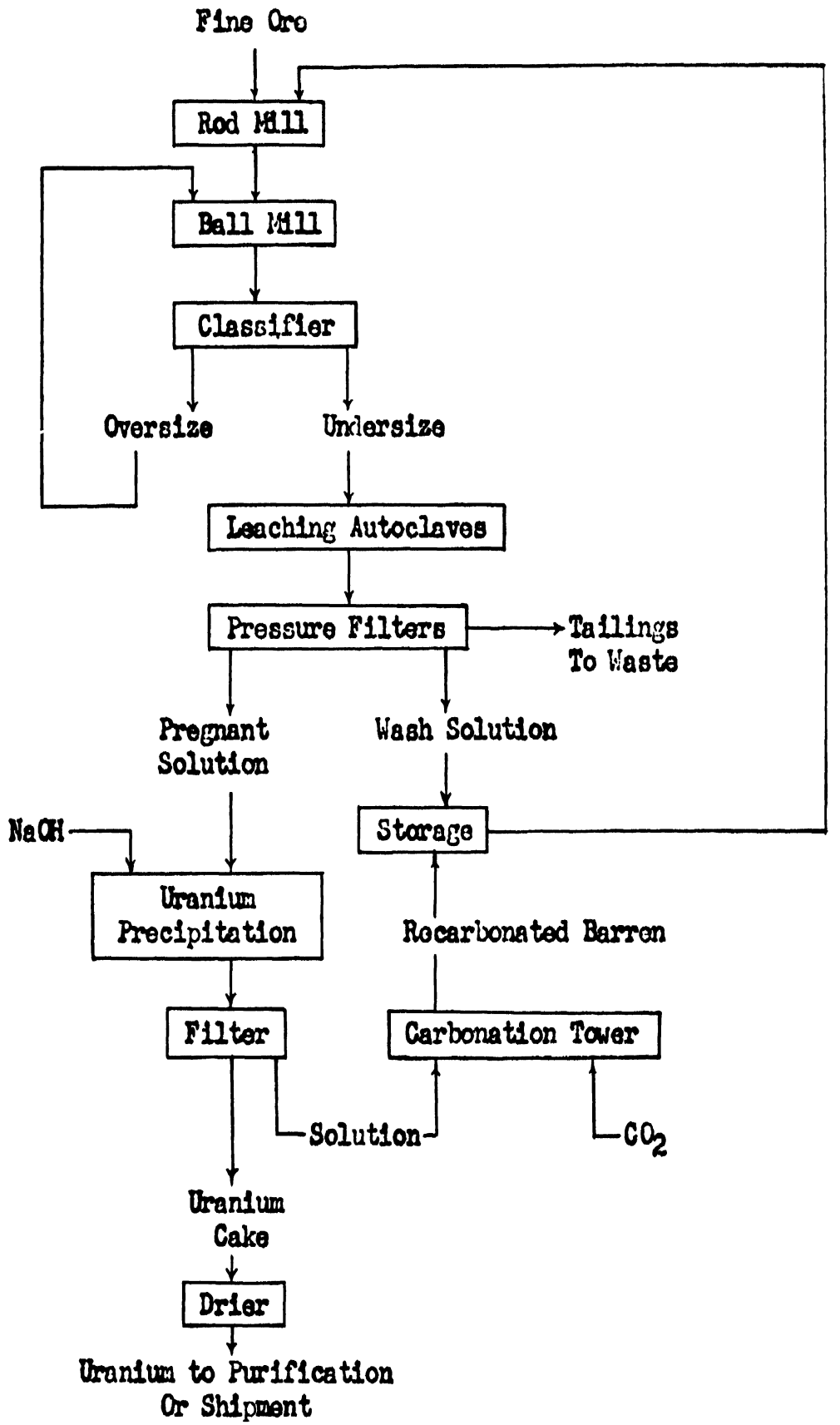

Figure 3. Flowsheet of raw leach for oxidized uranium of Anaconda Copper Mining Company, Grants, New Mexico

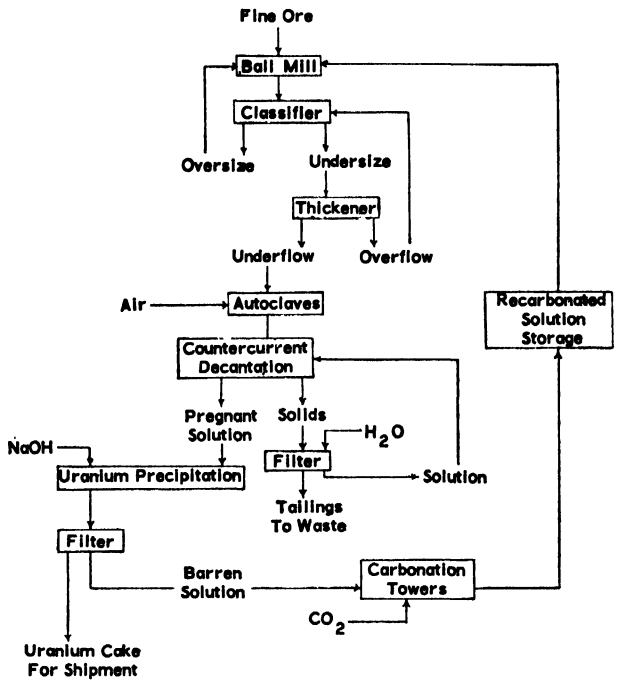

Figure 4. Flowsheet of raw ore leach for unoxidized or primary uranium of Eldorado Mining and Refining Limited, Beaverlodge, Saskatchewan

to precipitation where the uranium is precipitated as sodium diuranate by adding sodium hydroxide. The sodium diuranate precipitate is recovered by filtration in plate-and-frame presses.

The barren solution is recarbonated by contacting it with CO_2 from flue gas in a packed tower and the recarbonated solution is then re-used in the plant circuit.

Flowsheet for Leaching of Unoxidized or Primary Uranium Ores at the Beaverlodge, Saskatchewan, Plant of Eldorado Mining & Refining Limited[5]

Figure 4 shows the leaching and precipitation flowsheet of the Beaverlodge, Saskatchewan, mill. Following a normal crushing and sampling plant, the ore is stored in fine ore bins. The ore is discharged from the bins into the grinding circuit, where it is ground in ball mills operating in closed circuit with spiral classifiers. The grinding is done in a sodium carbonate solution. After grinding, the pulp is thickened to 60 per cent of solids and pumped to agitated autoclaves.

In the autoclaves, the slurry is held for 16 hours at a pressure of 110 pounds per square inch and a temperature of 104°C (220°F). During this cycle, air is passed through the autoclaves to oxidize tetravalent uranium to the hexavalent state. Leach solutions contain about 40 grams of carbonate and 20 grams of bicarbonate per liter.

The discharge from the autoclaves is sent to a countercurrent decantation circuit which is followed by drum filters to effect a liquid-solids separation.

The precipitation of uranium as the diuranate and the recarbonation of the barren solution are carried out in a manner similar to that described previously for the Grants, New Mexico, mill.

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The Carbonate Chemistry of Uranium: Theory and Applications

By L. A. McClaine, E. P. Bullwinkel, and J. C. Huggins,* USA

In recent years great interest has been shown in the leaching of uranium ores with carbonate solutions. Primarily as a result of this interest, uranium carbonate chemistry has been extensively studied in certain of its theoretical and practical implications. In this paper we shall review these implications and present a consistent picture of this phase of uranium technology. It is our hope that this review will contribute to a better understanding of the applications of carbonate systems to uranium extractive metallurgy. As will be evident, much further research is required in this field.

CARBONATE CHEMISTRY OF URANIUM

Solid Compounds

There are numerous solid carbonate compounds of uranium known. These comprise the parent hexavalent compound UO_2CO_3; salts of the tricarbonate complex ion, $[UO_2(CO_3)_3]^{4-}$ salts of the dicarbonate complex ion, $[UO_2(CO_3)_2(H_2O)_2]^{2-}$ (written arbitrarily with $2H_2O$ to preserve the *hexacoordination* of UO_2^{++}); as well as a sodium salt of the carbonate complex of uranium(IV), $Na_6U(CO_3)_5 \cdot 11$–$12\,H_2O$. Various methods for synthesizing these compounds are outlined in Table I. The references cited in this table should be consulted for further details.

Since most of these carbonate complex ions are only stable in alkaline solutions, it is to be expected that salts of these anions with highly charged cations (e.g., Al^{3+}, Fe^{3+}) are incapable of existence because of hydrolysis reactions.

Table II gives some solubilities for these solid salts. The alkaline earth salts are all unstable in the presence of carbonate solutions, according to the following equation:

$$M_2UO_2(CO_3)_3(s) + 2CO_3^{=} = [UO_2(CO_3)_3]^{4-} + MCO_3(s) \quad (1)$$

Of the solid compounds, $Na_4UO_2(CO_3)_3$ has been the most extensively investigated. Brown and Schnitt[1] investigated the solubility of $Na_4UO_2(CO_3)_3$ as a function of ionic strength in the solutions of various sodium salts. They found that this solubility at room temperatures (20–30°C) can be expressed quite well by the equation:

$$\log_{10} K_{sp} = 1.25\sqrt{\mu} - 2.2 \quad (2)$$

where μ is the *molal* ionic strength ($\frac{1}{2}\Sigma' m_i Z_i^2$) and K_{sp} is the *molal* solubility product of $Na_4UO_2(CO_3)_3$.

Bunce, Furman and Mundy[2] had earlier measured the solubility of $Na_4UO_2(CO_3)_3$ in $NaHCO_3$, Na_2CO_3, and Na_2SO_4 solutions at 30°, 60°, and 90°C. They demonstrated that the solubility of $Na_4UO_2(CO_3)_3$ is decreased both by increasing temperatures and ionic strengths. Their data are shown graphically in Fig. 1.

It should be mentioned that $Na_4UO_2(CO_3)_3$ is not rapidly precipitated from supersaturated solutions at room temperatures. This slow approach to equilibrium is illustrated in Fig. 2. Failure to appreciate this slowness of precipitation has led Bachelet, Cheylan, Douis, and Goulette[3] to erroneously postulate that the uranyl tricarbonate complex is present in solution as a hydrate which is only slowly converted at room temperatures to a less soluble anhydrous form.

Following the discovery of a laboratory method for preparing UO_2CO_3 by Miller, Pray, and Munger,[4] extensive work on the four component system UO_3–Na_2O–CO_2–H_2O was undertaken by Blake, Lowrie, Hill, and Brown.[5] The most interesting phase diagram from this excellent work is the three component system UO_2CO_3–H_2O–Na_2CO_3, shown in Fig. 3. We have modified their original diagram (dotted lines) to show the existence of $Na_2UO_2(CO_3)_2 \cdot xH_2O$ (solid) which has been prepared subsequent to their work. To make clear the narrow region, $Na_2UO_2(CO_3)_2 \cdot xH_2O$ (solid) + solution, in this diagram, the true loci of $Na_4UO_2(CO_3)_3$ (solid) and $Na_2UO_2(CO_3)_2 \cdot xH_2O$ (solid) have been spread apart.

It may be seen from this phase diagram that the solubility of $Na_4UO_2(CO_3)_3$ is decreased as the Na_2CO_3 concentration is increased. Also, the solubility of UO_2CO_3 in Na_2CO_3 solutions is given by a straight line, yielding equilibrium solutions have a CO_3/U ratio of 2. It is further noted that it is not possible to prepare UO_2CO_3 by evaporating any solution composition in this phase diagram.

The recently reported compound,[3] $Na_6[(UO_2)_2(CO_3)_5]$ and $Na_6[(UO_3)_3(UO_2)_2(CO_3)_5]$, would

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appear to be mixtures from a consideration of the preparatory methods employed. The first of these "compounds" is probably a mixture of $Na_4UO_2(CO_3)_3$ and $Na_2UO_2(CO_3)_3 \cdot xH_2O$, while the second is a complicated mixture of $Na_4UO_2(CO_3)_3$ and sodium uranates.

With respect to the use of UO_3 in preparing these "compounds" and in other reactions concerning carbonate solutions, it must be stressed that UO_3 is never a stable solid phase in the presence of solutions containing large concentrations of cations.[6] This instability is caused by the greater insolubility of uranates as compared with UO_3, e.g.,

$$UO_3 \cdot 2H_2O\ (s) + Na^+ \rightarrow \text{Na uranates} + H^+ \quad (3)$$

$$H^+ + UO_3 \cdot 2H_2O\ (s) \rightarrow \text{soluble } UO_2^{++} \text{ hydrolysis polymers} \quad (4)$$

The sodium uranates have been recently discussed by Ricci and Loprest.[7] The hydrolysis reactions of UO_2^{++} and the polymers formed have been carefully studied by Sutton;[8] cf. MacInnes and Longsworth,[10] Ahrland.[9]

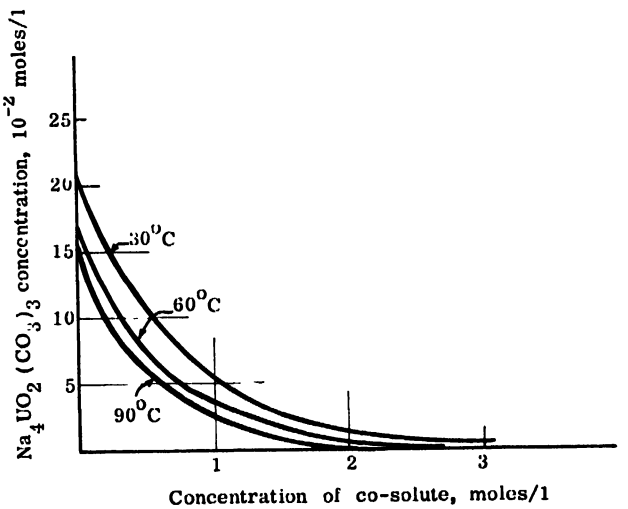

Figure 1. Solubility of $Na_4UO_2(CO_3)_3$ in sodium salt solutions at 30°C, 60°C and 90°C

Solution Equilibria Involving + 6 Uranium Carbonate Complexes

Previous work on the carbonate solution chemistry of uranium(VI) has been largely concerned with the identification of the complex ions present. Thus, Haldar [11] has noted two inflections in thermometric and conductometric titrations of UO_2^{++} solutions with $CO_3^=$ solutions. The inflections corresponded to CO_2/U ratios of 2 and 3 and he suggested the presence of a dicarbonate and tricarbonate uranyl complex. Bachellet, Cheylan, Douis, and Goulette[3] further demonstrated that when UO_3 is dissolved in *excess* HCO_3^-, the quantity of CO_2 gas evolved corresponds quite well with the following equation:

$$UO_3 \cdot 2H_2O\ (s) + 4HCO_3^- = [UO_2(CO_3)_3]^{4-} + CO_2\ (g) + 4H_2O \quad (5)$$

Halpern[12] carried out potentiometric titrations using

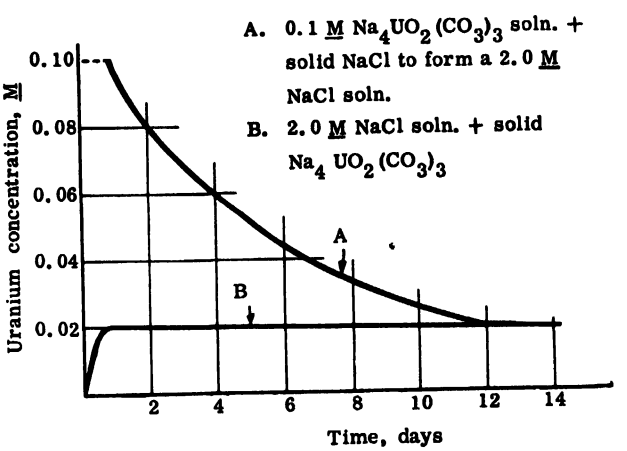

Figure 2. Approach to equilibrium solubility for $Na_4UO_2(CO_3)_3$

a glass electrode on standard carbonate solutions containing various amounts of UO_2^{++}. He showed that 3 moles of $CO_3^=$ per mole of UO_2^{++} were not available during the titration in the $CO_3^= - HCO_3^-$ range and only become available near the $HCO_3^- - CO_2$ endpoint. In addition, Blake, Lowrie, Hill and Brown[5] suggested that the solubility of UO_2CO_3 in Na_2CO_3 and $Na_4UO_2(CO_3)_3$ solutions to yield neutral solutions and CO_2/UO_3 ratios of 2 was indicative of the existence of a dicarbonate complex ion, $[UO_2(CO_3)_2]^{2-}$.

Recent work in our laboratory[13] has extended this earlier work and shown conclusively that in solution there are only two important carbonate complexes of uranium(VI), namely, a tricarbonate and dicarbonate complex. The following discussion is based on this work.

The tricarbonate complex, $[UO_2(CO_3)_3]^{4-}$, is stable in solution when the ratio of $CO_3^=$ to UO_2^{++} exceeds 3. When this ratio equals 3 [e.g., an aqueous solution of $Na_4UO_2(CO_3)_3$], this complex is somewhat hydrolyzed. This hydrolysis is apparent from the alkaline reaction and enhanced absorption spectra of such solutions. This spectral enhancement, which

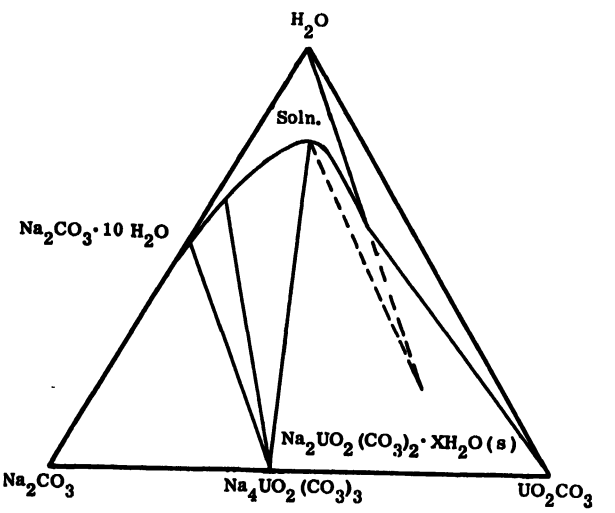

Figure 3. The system $Na_2CO_3 - UO_2CO_3 - H_2O$

is caused by the presence of intensely colored UO_2^{++} hydrolysis products, is illustrated in Fig. 4. When aqueous solutions of $[UO_2(CO_3)_3]^{4-}$ are diluted to low concentrations (~ 0.001 M), appreciable quantities of uranium precipitate as uranates.

The dicarbonate complex, $[UO_2(CO_3)_2(H_2O)_2]^{2-}$ is most readily prepared by saturating $CO_3^=$ solutions with UO_2CO_3. In open systems, such solutions readily lose CO_2 to form UO_2^{++} hydrolysis products and $[UO_2(CO_3)_3]^{4-}$. In the presence of excess HCO_3^- or $CO_3^=$, the dicarbonate complex is quantitatively converted into the tricarbonate complex. Absorption spectra for these two complexes in the absence of hydrolysis products is shown in Fig. 5.

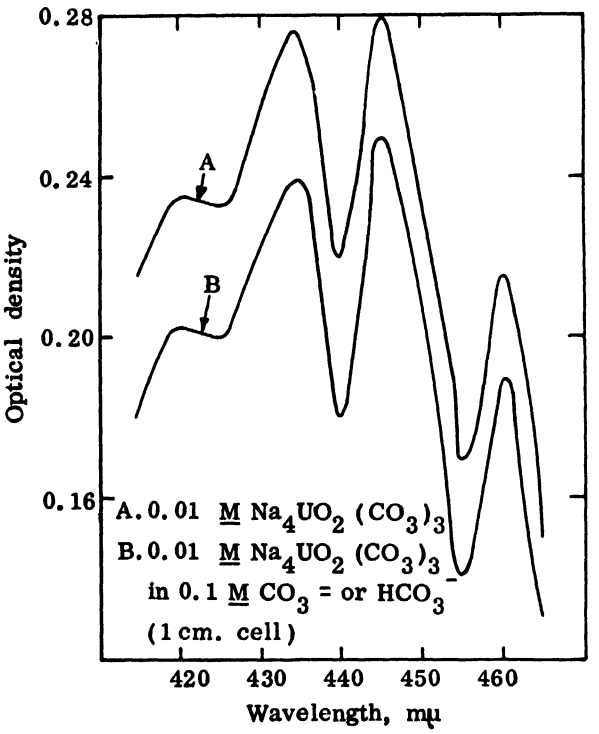

Figure 4. Spectra of $Na_4UO_2(CO_3)_3$ solutions

A qualitative picture of the equilibria connecting the two uranyl carbonate complexes is most easily obtained from the titration curve and spectral changes observed when aqueous $[UO_2(CO_3)_3]^{4-}$ solutions are treated with H^+, as shown in Figs. 6 and 7. (For comparison, a titration curve for Na_2CO_3 is included.) Noted along the $[UO_2(CO_3)_3]^{4-}$ titration curve by means of arrows are the ratios of moles of H^+ added to moles of U present. In Fig. 7 the H^+/U ratios associated with absorption spectra curves correspond to those indicated on the titration curve of Fig. 6. Curve A, which exhibits peaks at 420, 435, 445, and 460 mμ is characteristic of $[UO_2(CO_3)_3]^{4-}$. It is observed (curves B and C, Fig. 7) that upon addition of H^+, the 435 mμ peak remains constant, while the 420, 445, and 460 mμ peaks shift toward longer wave lengths. This shifting ceases at $H^+/U = 1$ (curve C) with the absorption peaks now occurring at 425, 435,

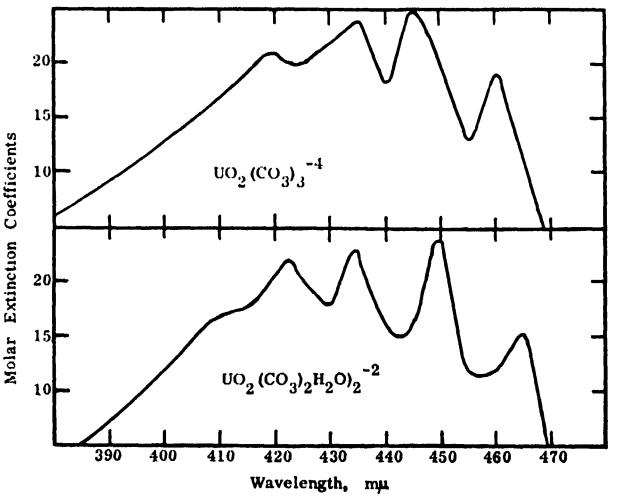

Figure 5. Absorption spectra of uranyl dicarbonate and tricarbonate complexes

450 and 465 mμ. These peaks are characteristic of the dicarbonate complex $[UO_2(CO_3)_2(H_2O)_2]^{2-}$. As the H^+ additions exceed $H^+/U = 1$ (curves D and E), the optical density of the solutions continuously increases at all wave lengths while the fine structure gradually disappears. Finally at $H^+/U = 3$ (curve F), the fine structure has been completely destroyed and replaced by a broad absorption band having a very large optical density in the 430–435 region (characteristic of UO_2^{++} hydrolysis products). Although not shown, further H^+ additions monotonously decrease the optical density of this broad band, and give finally at low pH's, the well-known spectrum of UO_2^{++}.

Turning now to the $[UO_2(CO_3)_3]^{4-}$ titration curve of Fig. 6, it is interesting to note that in the range $H^+/U = 0$ to $H^+/U = 1$, no evidence, such as an inflection, is seen of the transformation of the tricarbonate complex into a dicarbonate complex. The inflection shortly after $H^+/U = 3$ is probably due to the following reaction,[8]

$$[U_3O_8(OH)]^+ + H^+ = U_3O_8^{++} + H_2O \quad (6)$$

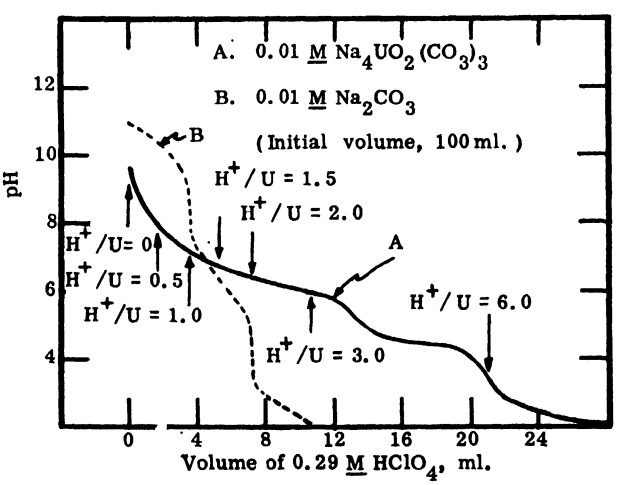

Figure 6. Titration curves for $Na_4UO_2(CO_3)_3$ and Na_2CO_3

while the inflection at $H^+/U = 6$ corresponds to the endpoint for the over-all reaction,

$$[UO_2(CO_3)_3]^{4-} + 6H^+ = UO_2^{++} + 3H_2O + CO_2(g) \quad (7)$$

The foregoing series of events is also observed when HCO_3^- solutions of $[UO_2(CO_3)_3]^{4-}$ are titrated except that the conversion $[UO_2(CO_3)_2(H_2O)_2]^{2-}$ is delayed as would be expected from considering the equation,

$$2H_2O + [UO_2(CO_3)_3]^{4-} + H^+ = [UO_2(CO_3)_2(H_2O)_2]^{2-} + HCO_3^- \quad (8)$$

By using $CO_2(g)$ as an acid instead of H^+, it has been possible to determine quite simply from spectrophotometric measurements the equilibrium constants for the following reactions,

$$[UO_2(CO_3)_2(H_2O)_2]^{2-} + 2HCO_3^- = [UO_2(CO_3)_3]^{4-} + CO_2(g) + 3H_2O \qquad K \approx 65 \quad (9)$$

$$UO_2CO_3(s) + 2HCO_3^- + H_2O = [UO_2(CO_3)_2(H_2O)_2)]^{2-} + CO_2(g) \qquad K \approx 26 \quad (10)$$

It should be noted that these reactions are free from side reactions and do not involve pH measurements.

From an investigation of the effect of CO_2 pressure, the constant for the following equilibrium,

$$UO_3 \cdot 2H_2O(s) + CO_2(g) = UO_2CO_3(s) + 2H_2O \quad (11)$$

was found to be approximately 10^4.

The foregoing equilibrium constants have been corrected for activities using Kielland's data.[14] By combining these constants with an estimate of the free energy of formation of $UO_3 \cdot 2H_2O$ and other available data,[15] the thermodynamic values given in Table III may be calculated. The free energy value for $UO_3 \cdot 2H_2O$ was estimated from the heat of formation of UO_3,[16] heats of solution of UO_3 and $UO_3 \cdot 2H_2O$,[17] and Latimer's estimate[18] for the

Table II. Aqueous Solubility of Some Uranium Carbonate Compounds

Compound	*Solubility (gm U/liter)*	*Reference*
$Na_4UO_2(CO_3)_3$	65 (room temp.)	1
$Na_2UO_2(CO_3)_2 \cdot xH_2O$	~350 (room temp.)	5, 13
UO_2CO_3	v. insoluble	4
$Ca_2UO_2(CO_3)_3 \cdot 10H_2O$	0.33 (0°C)	
	1.34 (23°C)	42
	3.68 (40°C)	
$Mg_2UO_2(CO_3)_3 \cdot 18H_2O$	39 (29°C)	
	41.5 (32°C)	42
	57.8 (42°C)	
$Ba_2UO_2(CO_3)_3 \cdot 6H_2O$	v. insoluble	42
$BaUO_2(CO_3)_2 \cdot xH_2O$	v. insoluble	13
$CaUO_2(CO_3)_2 \cdot xH_2O$	v. insoluble	13
$Tl_2UO_2(CO_3)_2 \cdot xH_2O$	v. insoluble	13
$(NH_4)_4UO_2(CO_3)_3$	23 (15°)	44
$K_4UO_2(CO_3)_3$	29 (15°)	44

Table I. Preparation of Uranium Carbonate Compounds

A. UO_2CO_3
1. $UO_3 + CO_2(g) \rightarrow UO_2CO_3$
Conditions: Water slurry of UO_3, 800–2500 psi CO_2, 100°C[4]; Reactive $UO_3 \cdot 2H_2O$ slurry, room temperature, atm pressure CO_2[13].
2. $UO_2^{++} + O_2 \rightarrow$ uranate
Uranate $+ CO_2 + H_2O \rightarrow UO_2CO_3 + [UO_2(CO_3)_2(H_2O)_2]^{2-}$
Conditions: Neutralize to pH 6–7.[13]

B. Alkali metal salts of $[UO_2(CO_3)_3]^{4-}$
1. Evaporate solutions containing constituent ions.
2. Precipitation by adding UO_2^{++} to concentrated alkali metal carbonate solutions, warming hastens the precipitation (see text).

C. Alkaline earth salts of $[UO_2(CO_3)_3]^{4-}$
1. Metathetical Reactions: e.g.
$2Ba^{++} + [UO_2(CO_3)_3]^{4-} \rightarrow Ba_2UO_2(CO_3)_3$.[43,42]

D. Salts of $[UO_2(CO_3)_2(H_2O)_2]^{2-}$
1. Saturate HCO_3^- solution with UO_2CO_3 and CO_2, then add excess of desired cation.[13]

E. $NA_6U(CO_3)_5 \cdot 11H_2O$
1. Chemical reduction:
Conditions: Agitate for several weeks in a sealed vessel an aqueous solution, 0.25*M* $Na_4UO_2(CO_3)_3$, 2.7*M* Na_2CO_3, and 0.3*M* $Na_2S_2O_4$.
2. Electrolytic reduction:
Conditions: Hg cathode-diaphragm cell, 26 cm^2Hg area — current 0.5 amp.; catholyte, 0.25*M* $CO_3^=$ — 0.36*M* HCO_3^-; for every 100 ml of this solution, reduce 0.05 moles $Na_4UO_2(CO_3)_3$. At the end of reduction, add 50 gm/liter of $Na_2CO_3 \cdot H_2O$ to salt out compound.

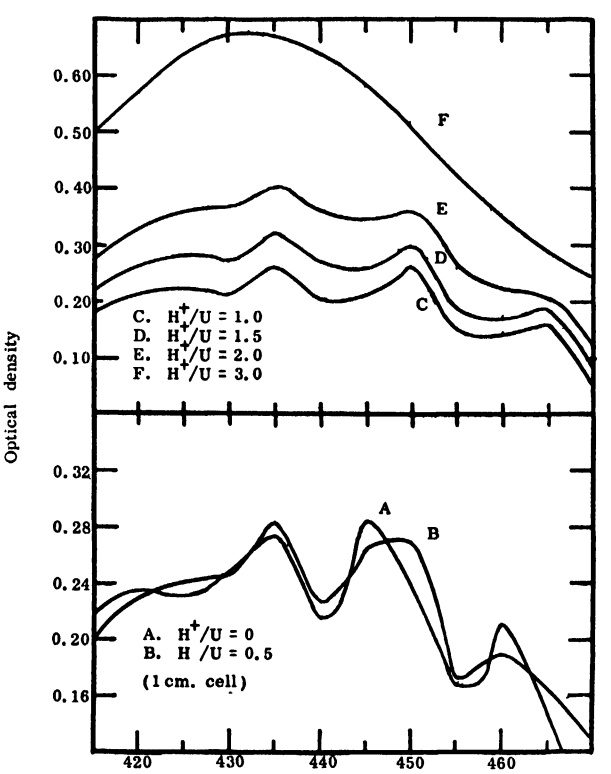

Figure 7. Spectra of $Na_4UO_2(CO_3)_3$ solution during H^+ titration

entropy contribution of water of hydration. It is difficult to assess the reliability of the data in Table III, but they should be sufficient for approximate calculations.

While UO_2^{++} and $CO_3^{=}$ are incapable of coexistence in solution, we may nevertheless calculate equilibrium constants for the formation of the uranyl dicarbonate and uranyl tricarbonate complexes. This calculation, using the free energies given in Table III, yields the following values:

$$UO_2^{++} + 2CO^{=} + 2H_2O = [UO_2(CO_3)_2(H_2O)_2]^{2-}$$
$$K \approx 4 \times 10^{14} \qquad (12)$$

$$UO_2^{++} + 3CO_3^{=} = [UO_2(CO_3)_3]^{4-}$$
$$K \approx 2 \times 10^{18} \qquad (13)$$

Table III. Free Energies of Formation

Compound	$-\Delta F^\circ$ *(kcal/mole)*
$UO_3 \cdot 2H_2O$	391
UO_2CO_3	377
$[UO_2(CO_3)_2(H_2O)_2]^{2-}$	622
$[UO_2(CO_3)_3]^{4-}$	640

The large values for these constants demonstrate the great stability of the uranyl carbonate complexes.

Oxidation-Reduction Reactions of Uranium in Carbonate Solutions

Besides the previously discussed uranyl carbonate complexes, there also exists a green uranium (IV) carbonate complex. This complex is formed when uranium(VI) carbonate solutions are reduced electrolytically or by means of powerful reducing agents (e.g., $S_2O_4^{=}$). It may also be prepared by the addition of uranous salts to carbonate solutions.[19] The absorption spectra of this complex is shown in Fig. 8. Also included in this figure is the absorption spectra of a mineral oil mull of the solid salt, $Na_6U(CO_3)_5 \cdot 11H_2O$, which is precipitated from reduced uranium carbonate solutions at high uranium and carbonate concentrations (see Table I). The agreement between the absorption spectra of the solution and solid is striking.

It is of interest to note that both Th(IV) and Ce(IV) have been reported[20] to form carbonate complexes of the type $M_6X(CO_3)_5 \cdot 12H_2O$. It is not known at present what the true formula of the uranium(IV) carbonate complex is in solution. While from a coordination and charge standpoint $[U(CO_3)_5]^{6-}$ seems excessive, we shall nevertheless adopt this formula for convenience in the following discussion.

As would be expected from the very low solubility of $U(OH)_4$ ($K \approx 10^{-45}$), $[U(CO_3)_5]^{6-}$ is only stable in solutions[18] containing excess HCO_3^- or $CO_3^{=}$. When OH^- or H^+ is added to such solutions, $U(OH)_4$ is precipitated. There is some doubt as to whether or not this hydrous oxide contains carbonate.) We have ascertained that this precipitation is reversible when performed at room temperatures.

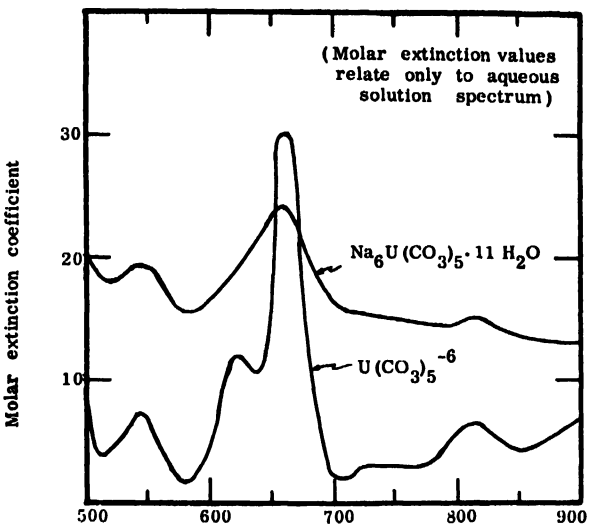

Figure 8. Absorption spectra for the uranium(IV) carbonate complex

Of great interest is the fact that when carbonate solutions containing both uranium(IV) and (VI) are treated with OH^- in the cold or are heated to temperatures exceeding 70–80°C, a dense black precipitate is thrown down. The nature of the precipitate is unknown except for the fact that it contains, by analysis, both uranium(IV) and (VI). It is therefore not UO_2 or a UO_2 hydrate. Perhaps it may be best described as a "mixed oxidation state" compound (see, however, below).

In preliminary potential measurements on various carbonate-bicarbonate solutions containing uranium (IV) and (VI), we have observed that the oxidation-reduction reaction

$$4OH^- + [U(CO_3)_5]^{6-} = [UO_2(CO_3)_3]^{4} + 2CO_3^{-=} + 2H_2O + 2e \qquad (14)$$

appears to be reversible at a variety of inert metal electrodes (e.g., Hg, Pt, Cu). Likewise, reduction of uranium(VI) to uranium(IV) in $CO_3^{=}$–HCO_3^- solutions at various metal cathodes appears to proceed smoothly and at high current efficiencies, especially when the current density is very low. These results are quite surprising since one would expect a very large activation energy for a reaction as complicated as 14. This is especially so in view of Crandall's work[21] which demonstrates how tightly the two oxygens are bonded to the uranium in UO_2^{++}.

The simplest explanation for the apparent reversibility of reaction 14 is that the *actual* electrode reaction is a simple, one electron change involving uranium(V) and (VI) carbonate complexes, e.g.,

$$[UO_2(CO_3)_3]^{5-} = [UO_2(CO_3)_3]^{4} + e \qquad (15)$$

By analogy with the situation in acidic noncomplexing media,[22] we would expect that this (V) complex would be in equilibrium with the uranium(IV) and

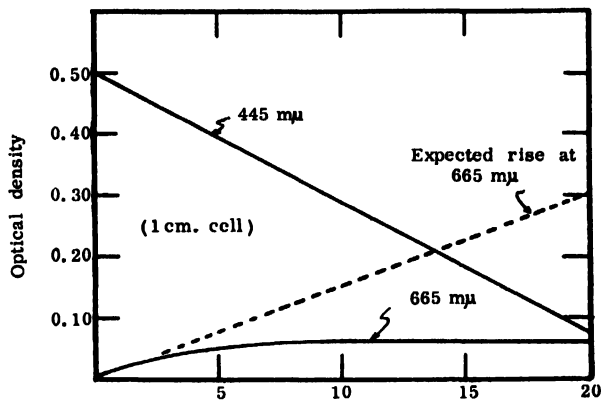

Figure 9. Spectral changes during electrolytic reduction of uranium(VI) carbonate solution

(VI) carbonate complexes by means of a disproportionation reaction, e.g.,

$$2CO_3^{-} + 2H_2O + [2UO_2(CO_3)_3]^{5-} = [U(CO_3)_5]^{6-} + [UO_2(CO_3)_3]^{4-} + 4OH^- \quad (16)$$

In contrast to the very small concentrations of +5 uranium obtainable at equilibrium in acid solutions, we believe that rather large equilibrium concentrations of this oxidation state may be obtained in carbonate solutions under suitable conditions. Unfortunately at present, experimental evidence in support of this belief is quite meager. Nevertheless we may consider some of our work concerning the (V) oxidation state of uranium in carbonate solutions. [See also Harris and Kolthoff[19] for polarographic studies which give evidence for the existence of uranium(V) in carbonate solutions.]

As would be expected from the large OH^- dependence shown in Equation 16, the uranium(V) complex should be most stable in carbonate solutions of high pH. This expectation is realized by following visually the color changes which occur when $[UO_2(CO_3)_3)]^{4-}$ in various HCO_3^- $CO_3^=$ mixtures is reduced electrolytically. For example, when $[UO_2(CO_3)_3]^{4-}$ in HCO_3^- solution is reduced, it is observed that the bright yellow of the (VI) complex is gradually replaced by the green color of the (IV) complex. However, when $CO_3^=$ solutions (containing small amounts of HCO_3^-) of $[UO_2(CO_3)_3]^{4-}$ are reduced, it is observed that the yellow color gradually fades to yield an almost colorless solution. Thereafter the green color of the (IV) complex slowly becomes apparent. [The (V) state of uranium would be expected to be essentially colorless by analogy with NpO_2^+ and PuO_2^+]

A more quantitative picture is obtained by removing samples of the solution during the electrolysis and determining optical densities (at 445 mμ and 665 mμ) and the number of reducing equivalents present. The optical density at 665 mμ is proportional to the concentration of the uranium(IV), while the optical density at 445 mμ may, without too much error, be considered to be proportional to the concentration of the uranium(VI). A typical plot of these optical densities versus reducing equivalents present is shown in Fig. 9 for a solution that was initially 0.02*M* $[UO_2(CO_3)_3]^{4-}$, 1.0*M* $CO_3^=$, and 0.08*M* HCO_3^-. It is apparent from the discrepancy between the expected (dotted line) and observed increase in optical density of the 665 mμ wave length that a colorless uranium intermediate is being formed during the reduction.

Further evidence for the stability of uranium(V) is the spectral changes observed when carbonate solutions of uranium(IV) and a similar solution of uranium(VI) are mixed. Such changes are shown in Fig. 10 as a function of time after mixing. It is seen from this figure that the uranium(IV) and (VI) are slowly reacting to form what must be uranium(V). (It was determined that the reducing equivalents present remained constant during this experiment.)

It is extremely tempting to relate in some way the black precipitates, previously discussed, with the presence of uranium(V) in carbonate solution. In this regard, it is of interest to note that Lydén[23] claims that the reaction of U_3O_8 in hot HCO_3^- solutions proceeds according to the equation,

$$U_3O_8(s) + 4HCO_3^- = [UO_2(CO_3)_3]_4^- + U_2O_5(s) + CO_2(g) + H_2O \quad (17)$$

Unfortunately, no X-ray studies were made on this solid residue. While the existence of U_2O_5 at high temperatures is questionable,[24] it would seem that this would not preclude the existence of such a compound at room temperature.

While we are unable to give oxidation potentials connecting the various uranium couples in carbonate solution, we may calculate from available data (Table III and Ref. 15) the following half reaction potentials (for sign conventions see Latimer[18]).

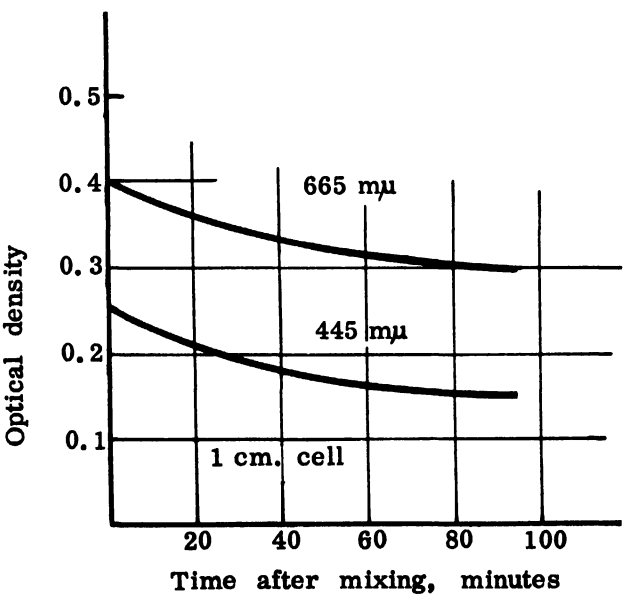

Figure 10. Spectral changes on mixing uranium(IV) and (VI) carbonate solutions

$$UO_2(s) + 3CO_3^{=} = [UO_2(CO_3)_3]^{4-} + 2e, \quad E^0 = 0.32\text{ v} \qquad (18)$$

$$U(OH)_4(s) + 3CO_3^{=} = [UO_2(CO_3)_3]^{4-} + 2H_2O + 2e, \quad E^0 = 0.50\text{ v} \qquad (19)$$

$$U_3O_8(s)\ 2H_2O + 9CO_3^{=} = 3[UO_2(CO_3)_3]^{4-} + 4OH^- + 2e, \quad E^0 = 0.35\text{ v} \qquad (20)$$

The free energy of formation of UO_2 and U_3O_8 were calculated from the new heats of formation of these oxides given by Huber.[25] The free energy of $U(OH)_4$ was obtained from Latimer.[18]

Structure of Uranium Carbonate Compounds

While UO_2CO_3 is the only uranium carbonate compound which has been investigated structurally, we may nevertheless discuss in a general fashion the structure of these compounds by drawing on the extensive structural information available for other uranium and actinide element compounds.[26,27] This discussion will be limited to uranium(VI) carbonate compounds because nothing is known about the *actual* number of carbonate ions associated with the uranium(IV) in $Na_6U(CO_3)_5 \cdot 11H_2O$.

From X-ray studies of solid uranium(VI) compounds, such as UO_3, UO_2F_2 and $CaUO_4$, it is found that distinct linear uranyl (OUO) groups exist, each being surrounded by a puckered ring of six neighboring atoms of either O or F. This hexacoordinating ring lies normal to the OUO axis and in the plane of the uranium. A similar coordination is also observed[28] in the complex salt, $RbUO_2(NO_3)_3$. In this compound there is a linear arrangement of uranium, oxygen, and rubidium such as . . . OUO . . . Rb . . . OUO . . . Rb, while three nitrate ions surround each uranium and lie normal to the Rb . . . OUO . . . Rb axis. These planar, triangular NO_3^- groups each supply two oxygen neighbors to the uranium to provide hexacoordination.

From this structure of $RbUO_2(NO_3)_3$ and the great similarity between NO_3^- and $CO_3^{=}$ ions, it is reasonable to assume that the structure of $[UO_2(CO_3)_3]^{4-}$ comprises a linear UO_2^{++} surrounded at its equator by 3 $CO_3^{=}$, each $CO_3^{=}$ supplying two oxygen neighbors to the uranium. [This structure is in accord with coordination observed[29] in the monocarbonate complex salts of +6 plutonium(V) and americium(V).] Thus, solid uranyl tricarbonate salts would be ionic crystals made up of cations and discrete $[UO_2(CO_3)_3]^{4-}$ anions. Similar considerations apply to the uranyl dicarbonate complex, where two waters may be included in the complex anion formula to provide hexacoordination.

Uranyl carbonate has been reported[30] to have a layer structure in which each UO_2^{++} is surrounded by four $CO_3^{=}$ ions; two of the $CO_3^{=}$ supply a pair of coordinating oxygens, while the other two supply only one oxygen apiece. We can see no reason why this compound does not crystallize in a more simple form with each UO_2^{++} being surrounded by three equivalent $CO_3^{=}$ ions, which are shared[13] among three UO_2^{++}.

THE CARBONATE LEACHING OF URANIUM ORES

Introduction

Carbonate leaching is advantageous in the processing of uranium ores because of its selectivity for dissolving uranium minerals while attacking very few other ore components. On account of its selectivity, reagent consumption is low and relatively pure uranium solutions are obtained. Uranium can be readily recovered from the leach solutions under conditions that enable the solution to be recycled for further leaching.

In spite of the advantages of carbonate leaching, it has not always been possible to compete with acid leaching on the basis of maximum uranium recovery from the ores. In some cases the fault has been in the manner of application. Our objective at this point is to briefly discuss some of the factors which must be recognized in order to achieve maximum uranium extractions with a carbonate leach.

Distribution of Uranium Minerals in the Ore

It must be recalled that carbonate solutions attack very few ore components other than the uranium minerals and therefore any uranium surrounded by gangue minerals in the ore particles will not be leached. Thus when using a carbonate leach, it is necessary to grind the ore sufficiently fine to liberate the desired percentage of uranium mineral. The grind required will vary depending on the ore. On the Colorado Plateau some ores are sandstones in which the uranium minerals are found with the material cementing together the sand grains. Such ores require grinding only to the sand grain size to liberate the uranium. At the opposite extreme are found limestone ores in which the uranium minerals are present as intergrowths and inclusions with calcite and fluorite.[31] In these ores we find that the finer the grind, even to the extent of pulverization to micron size, the greater the extraction possible.

Chemical Nature of Uranium Minerals

In the course of our work with Colorado Plateau ores we have attempted to gain information on the chemical properties of uranium minerals. These properties of uranium minerals have been generally neglected and we have found little helpful information in the literature. From the standpoint of the chemical constituents the uranium minerals have been classified[32] as arsenates, carbonates, molybdates, niobates-tantalates-titanates, oxides, phosphates, silicates, sulfates and vanadates. From our studies to date, we may generalize that the simple and complex arsenate, carbonate, molybdate, phosphate, sulfate, and vanadate minerals of hexavalent uranium are all readily soluble in carbonate leach solutions. The silicate minerals, however, because of their complex polymeric nature, can be expected to dissolve with difficulty in carbonate leach solutions. The dissolution would be favored by high pH and temperature,

which conditions promote the depolymerization and solubility of silicates. In our studies of uranophane mineral specimens we observe that uranophane dissolves slowly and apparently incompletely in carbonate leach solution. The presence of oxidants is not beneficial. Coffinite, reportedly a basic uranous silicate mineral, has also been studied. We find that with the use of oxidants this mineral can be dissolved in carbonate leach solution.

The simple oxide minerals of hexavalent uranium are readily soluble in carbonate solutions. The quadrivalent oxides and mixed oxides can be dissolved completely only with the use of oxidants. The rate of solution of these reduced oxides in the presence of oxidants appears to be greater for the uraninite samples from Colorado Plateau ores than for uraninite samples from vein deposits in Canada. In view of the known variation in reactivity of the uranium oxides with their method and conditions of preparation[6] this difference in rate is not surprising. It might be expected to vary to some extent for each individual ore deposit. Similar differences in reactivity might also be expected for minerals other than the oxides.

Uranates are included under the classification of oxides. We have not studied any mineral specimens identified as uranates or any ores reported to contain them. However, we have made in the laboratory the uranates of several metals. Many of these fail to dissolve in carbonate leach solution. In some cases the refractory uranates can be solubilized by the addition to the leach solution of some reagent which will solubilize the cation. For example $PbUO_4$ is essentially insoluble until ethylenediamine tetraacetic acid is added to the leach solution. This behavior may indicate that an insoluble lead carbonate film, formed on the surface of the compound, retards its solution. Since uranates generally cannot be precipitated from a carbonate leach solution of uranium under the conditions of its use, this implies that the failure of uranates to dissolve is due to the presence of some such rate inhibiting factor as an insoluble surface film.

The complex niobates-tantalates-titanates might be expected to be refractory in carbonate solutions to a greater extent than silicates. These minerals are most frequently found in pegmatite ores, which are not of any importance at present as a source of uranium. We have had no experience with these minerals.

Chemical Behavior of Uranium Minerals on Roasting Uranium Ores

The above generalizations with regard to the solubility of various minerals do not necessarily apply when the ores have been roasted prior to leaching. In the past such roasting has frequently been employed in milling operations to either improve filtering characteristics or to improve vanadium extractions from carnotite type ores.

It is well known that UO_2 and UO_3 react readily and at relatively low temperatures with basic oxides and some of their salts to form uranates.[6] Undoubtedly, many of the complex uranium minerals will react in the same manner. Thus the formation of uranates, which as we mentioned above are frequently insoluble or difficultly soluble in carbonate solution, probably accounts for the refractory nature of many uranium ores to carbonate leaching following roasting. We have observed in working with uraninite specimens containing from 4.5–60% U_3O_8, that, following a roast at 500°C in air, uranium extractions are slightly higher than before roasting. However, after such a roast the total extractions obtained with the use of an oxidant are not as great as those obtained from the unroasted ore. Following an air roast at 850°C, extractions were very low and oxidants were ineffective in increasing them. The only exceptions to these results were cases in which a large quantity of vanadium was closely associated with the uranium. In these cases the roasted minerals were readily soluble in carbonate leach.

Titrations of acid solutions of the samples following roasting indicate that in all cases only hexavalent uranium is present. Thus the uraninite has reacted during the roast with other components of the ore, probably to form uranates in the cases in which a refractory nature appeared and to form soluble uranyl vanadates in the samples with high vanadium content. The effectiveness of excess V_2O_5 during roasting in improving subsequent uranium extractions has been demonstrated by workers at Battelle Memorial Institute.[33] These workers further showed that other acidic oxides such as P_2O_5 are equally beneficial. The addition of V_2O_5 to ores prior to roasting to improve subsequent uranium extractions has been used in mill practice.[34]

One uraninite sample, obtained from a pegmatite ore, and concentrated to 78% U_3O_8, was sufficiently free from components other than uranium that it behaved on roasting as one would expect of UO_2. That is, reduced uranium was still present after roasting at 850°C and the use of oxidants did increase extractions from the roasted mineral.

A great deal more study to completely explain the high temperature behavior of uranium minerals, both alone and in the presence of other ore constituents, is required. We hope that the foregoing comments serve to emphasize the need for considering the chemical nature of the uranium minerals in the processing operations to which the ore is subjected prior to the application of the carbonate leach.

Nature of the Carbonate Leach Solution

An important factor affecting the extraction of uranium from ores is the pH of the carbonate leach solution. The solubilization of a hexavalent uranium mineral, such as carnotite, and a quadrivalent uranium mineral, such as uraninite, may be represented by the following equations:

$$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O + 6CO_3^{=} = 2K^+ + 2[UO_2(CO_3)_3]^{4-} + 2VO_3^- + 4OH^- + H_2O \quad (21)$$

$$2UO_2 + 6CO_3^- + 2H_2O = 2[UO_2(CO_3)_3]^{4-} + 4OH^- \quad (22)$$

The above equations demonstrate that hydroxide ion is formed in the dissolving reactions. Since uranates will precipitate when the hydroxide ion concentration becomes sufficiently high, according to the equation:

$$2[UO_2(CO_3)_3]^{4-} + 6OH^- + 2Na^+ = Na_2U_2O_7 + 6CO_3^= + 3H_2O \quad (23)$$

some bicarbonate is generally required in the leach solution to remove this hydroxide ion and thereby prevent any uranate formation.

Another important factor to consider is the maintenance of oxidizing conditions in the leaching process. As we have previously mentioned, oxidants are essential in order to achieve the solution of reduced uranium minerals. Oxidants may also be required if reducing substances are present in the ore or introduced during the processing operations. Table IV illustrates the different uranium extractions obtained by carbonate leaching (with no oxidant present) of an ore following grinding in an iron ball mill as compared with grinding in a porcelain ball mill. These data demonstrate that reducing conditions in the leach solution, such as that caused by finely divided iron picked up in the milling operation, are capable of decreasing the uranium extractions from an ore. Aeration of the solution during leaching is capable of overcoming this effect from grinding in an iron ball mill.

Table IV. Effect of Grinding Procedure on Uranium Extractions Obtained from Utex Ore by Carbonate Leaching*

Grinding conditions			*Per cent uranium extractions*
Ball mill	*Media*	*Mesh size*	
Iron	Water	−100	83
Iron	Water	−200	24
Porcelain	Water	−100	90
Porcelain	Water	−200	92

* Leaching conditions: Ground unroasted ore contacted for 18 hours with 0.5*M* Na_2CO_3 - 0.5*M* $NaHCO_3$ solution at 90° C.

From the oxidation potentials given for Equations 18, 19, and 20, it is apparent that weak oxidizing agents should suffice for oxidizing reduced uranium oxides. However, from a practical standpoint the oxidant selected must be inexpensive and rapid in its action.

From the standpoint of rapidity we find that MnO_4^- is the best oxidant while from the standpoint of cost air appears most desirable. Because of its economic advantages, some detailed studies of air oxidation have been carried out by various investigators. Workers at the Canadian Department of Mines have investigated the process applications of air oxidation at atmospheric pressures. Such atmospheric aeration requires long retention times (e.g., 48 hours) to achieve complete oxidation.

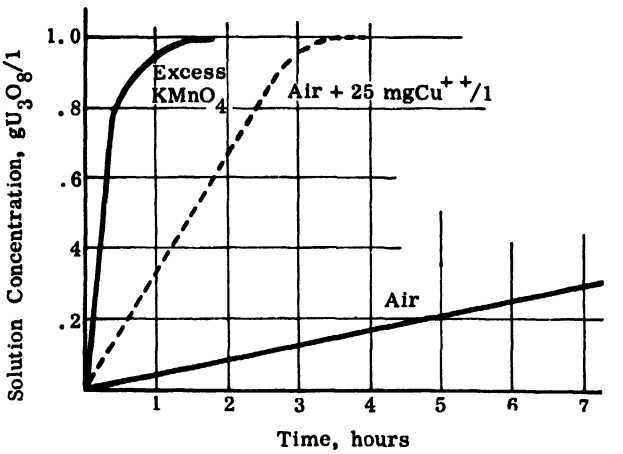

Figure 11. Dissolution of U_3O_8 in 0.5M Na_2CO_3 — 0.5M $NaHCO_3$ solution using air oxidation with and without Cu^{++} present

These retention times may be materially shortened (e.g., to four hours) by the use of high pressure leaching as demonstrated by workers at the University of British Columbia.[35,36]

In our laboratory we are currently investigating the use of catalysts to speed up the air oxidation of reduced uranium minerals without resort to high pressures. Figure 11 demonstrates recently obtained results on the effectiveness of Cu^{++} in increasing the rate of air oxidation of the compound U_3O_8 at atmospheric pressure. Also included in this figure for comparison is the dissolution curve obtained using MnO_4^- as an oxidant.

RECOVERY OF URANIUM FROM CARBONATE LEACH SOLUTION

General

There are two methods presently in commercial use for the recovery of uranium from carbonate solutions. A method used on solutions containing both uranium and vanadium is to acidify the solutions to a pH of approximately 6. At this point a "synthetic carnotite" (sodium uranyl vanadate) precipitates. This precipitate is fused with soda ash, salt, and sawdust to form UO_2 and sodium vanadates. A marketable UO_2 product is obtained by leaching out the soluble sodium vanadate from the fused mass. The filtrate from the uranium precipitation is heated and acidified further to a pH of approximately 2.5 where a vanadium oxide, "red cake", precipitates.

The other process for precipitation of uranium is applied to solutions containing little or no vanadium and makes use of a base to precipitate a uranate. It has been found that high concentrations of vanadium interfere with the precipitation of the uranate. More detailed descriptions of these processes may be found in the literature.[33,37,38,39]

Development work has been conducted on processes for removing the vanadium prior to caustic precipitation of uranium. These processes are based upon the use of an inorganic cation to precipitate an insoluble

vanadate. The principal ions used have been Fe^{++} and Pb^{++}. The use of Pb^{++} appears to offer definite advantages over that of Fe^{++} since lead sulfate may be recovered and recycled by leaching the lead vanadate with sulfuric acid. The acid leach may then be heated to precipitate V_2O_5. Use of ferrous sulfate has the objection that extensive formation of $FeCO_3$, $Fe(OH)_2$ or $Fe(OH)_3$ does occur, when vanadium concentrations are low, thereby resulting in high reagent consumptions and incomplete vanadium precipitation.

Reduction of Uranium and Vanadium in Carbonate Solutions

Uranium may be reduced by suitable reducing agents to the uranous carbonate complex as suggested by Equation 24:

$$[UO_2(CO_3)_3]^{4-} + 2CO_3^{=} + 2H_2O + 2e^- = [U(CO_3)_5]^{6-} + 4OH^- \quad (24)$$

At higher pH's and temperatures, this complex will decompose to the green uranous hydroxide according to Equations 25 and 26.

$$[U(CO_3)_5]^{6-} + 4OH^- = U(OH)_4 + 5CO_3^{=} \quad (25)$$

$$[U(CO_3)_5]^{6} + 4H_2O \overset{heat}{=} U(OH)_4 + 4HCO_3 + CO_3^{=} \quad (26)$$

If the conditions of high pH or high temperature are present during the reduction reaction, it appears that a hydrated mixed oxide is formed, e.g., $U_3O_8 \cdot xH_2O$, although some investigators[40] believe the compound to be uranous oxide, UO_2.

In the event that vanadium is also present, it will be reduced concurrently with the uranium. Vanadium (V) is reduced to the (III) state and precipitated as the vanadic hydroxide $V(OH)_3$ or the oxide[41] V_2O_3 according to Equations 27 or 28.

$$VO_3 + 3H_2O + 2e^- = V(OH)_3 + 3OH^- \quad (27)$$

$$2VO_3 + 3H_2O + 4e^- = V_2O_3 + 6OH^- \quad (28)$$

The reduction of vanadium is a consecutive reaction with a soluble vanadium(IV) species as an intermediate. A typical rate curve for this reduction is shown in Fig. 12. The reducing agent was sodium amalgam. The data were obtained by titrating, electrometrically, an acidified aliquot of filtered solution with $KMnO_4$ to obtain the concentration of vanadium(IV) and then back-titrating with $FeSO_4$ to obtain the total vanadium present. The difference between the initial vanadium concentration and the total in solution as found by titration gave the amount of vanadium(III) precipitated. The rate of the reduction of (V) to (IV) is approximately first order if the induction period is neglected.

Several reducing agents such as sodium dithionite ($Na_2S_2O_4$), zinc and ammonia, and zinc and cyanide have been tried on a laboratory scale for the reduction of uranium in carbonate solutions. Although, in general, these methods appear to be satisfactory, they do not appear to be economically feasible and they have the added disadvantage of introducing impurities which may possibly impair the effectiveness of the leach solution upon recycling.

The Hydrogen Reduction Process

Forward and Halpern[40] developed a method of reduction by hydrogen in the presence of a nickel catalyst. It was found that the rate of precipitation was directly proportional to the amount of nickel and to the square root of the partial pressure of hydrogen. For a practical operation, temperatures of 100–150°C and hydrogen partial pressures of 50–200 psi are recommended with the amount of catalyst variable to control the rate. The amount of catalyst would normally be in the range of 3–10 gm/l. Although the process has the disadvantage of being a pressure operation this is offset to a certain extent by a rapid rate of precipitation. The advantage of this process is that no contaminating agents enter the solution and the nickel may be recovered readily by a magnetic separator.

The Sodium Amalgam Reduction Process

A reducing agent that has been investigated quite widely in the United States and Canada is sodium amalgam. The advantage of the amalgam is that the mercury has a high hydrogen over-voltage and very dilute solutions of sodium in mercury will not decompose water in strongly basic solution. For an efficient operation, it is important that the side reaction of the amalgam and water be minimized. Conditions necessary to reduce the reaction between the sodium and water are a low concentration of sodium in amalgam, low temperature, high pH, and vessels containing the amalgam and solution must be fabricated from non-conducting material. In general, amalgams containing on the order of 0.02% by weight sodium and operating temperatures of approximately 25°C appear to be most suitable for a production operation on the usual leach solutions. Under these conditions, sodium efficiencies, i.e., ratio of equivalents of material reduced to the equivalents of sodium expended, on the order of 80% may be obtained.

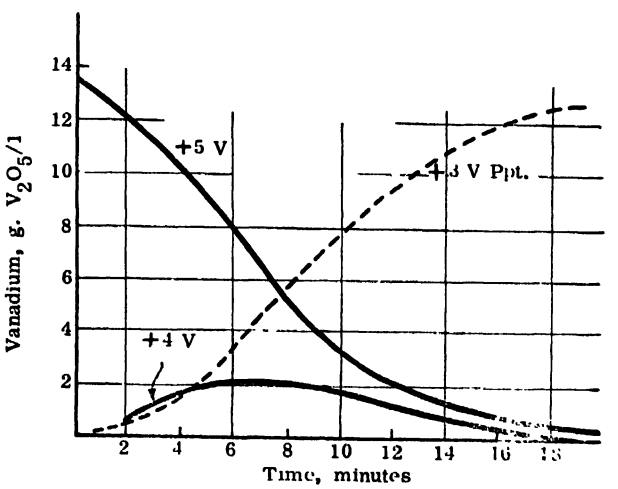

Figure 12. Sodium amalgam reduction of vanadium in carbonate solution

The rate of reaction between the amalgam and the uranium in the solution is proportional to the surface area of the amalgam and therefore all types of contactors have as their objective a fine dispersion of amalgam throughout the solution. Several contactors including an amalgam spray tower, a packed tower with countercurrent flow of solution and amalgam, and various types of agitators acting in an amalgam pool have been investigated. The foregoing methods are all satisfactory, but care must be taken during the operation to avoid flouring the mercury.

Amalgam may be produced either electrolytically from brine or by direct combination of sodium and mercury under controlled conditions, but the economics favor electrolytic production.

The Electrolytic Reduction Process

Chemical reduction of the uranium as a recovery method led naturally to the investigation of electrolytic methods. The classical method for the production of amalgam is the mercury cathode cell and, since the amalgam was found to be capable of reducing the uranium and/or vanadium, the mercury cathode cell was one of the first cells tried. As has been explained previously in this paper, both uranium and vanadium go through a soluble intermediate stage during reduction and, therefore, a diaphragm is required in the cell. The function of the diaphragm is to minimize migration of the soluble reduced compounds to the anode where they would undergo oxidation. In this respect the cell used for reduction differs from the conventional mercury cathode cell since no diaphragm is necessary in the production of caustic soda. Other principal differences are that the mercury is not cycled through the cell and that the solution is agitated. Most of the common diaphragm materials, such as canvas, alundum, and asbestos are satisfactory except when solutions obtained from salt roasted ores are used. Then the Cl_2 or ClO^- formed attacks canvas. The development of ion exchange membranes, particularly the cation type of membrane, offers a good diaphragm material since the reduced compounds are present as anions and will not be exchanged by the cation exchanger hence migration is prevented theoretically.

It was found that for a given current the rate of precipitation, or current efficiency, increases with decreasing cathode current density, increasing temperature, agitation, and uranium concentration. In the case of reduction by amalgam it was found that increased temperature lowered the hydrogen over-voltage which led to inefficient operation. However, in electrolysis the increased rate of reduction with temperature offsets the decrease in hydrogen over-voltage. A further advantage of elevated temperatures is that the cell voltage is lower for a given current flow, thus reducing power consumption. In the case of carbonate solutions containing only uranium it is usually necessary to accompany the reduction with heating in order to break up the soluble (IV) carbonate complex and precipitate uranium. However, if the electrolysis of cold solutions is carried far beyond the point for complete reduction of uranium, sufficient hydroxide will be generated to precipitate $U(OH)_4$. When vanadium is present it appears that sufficient hydroxide is liberated during the reduction of vanadium (see Equations 27 or 28) to precipitate $U(OH)_4$, and therefore the electrolysis may be conducted at room temperatures.

Preliminary cost estimates indicate that optimum operating conditions are achieved using cathode current densities of 0.3 to 0.5 amp/in^2 and temperatures of approximately 80°C.

Some investigators have tried cathode materials other than mercury and the results have been inconclusive. Workers at Rohm and Haas have reported that uranium may be reduced in carbonate solutions by platinum, graphite, or copper cathodes. On the other hand, workers at American Cyanamid Company and The Merrill Company reported that only water is reduced by cathodes of materials other than mercury; this reduction of the water liberates sufficient OH^- to bring about precipitation of the sodium uranates. The problem of reducing uranium at these other cathode materials appears quite complex since it involves adjusting the operating variables such as pH, temperature, cathode current density, and cathode potential. A qualitative picture may be obtained from Fig. 13 which shows the effect of increased current densities on the reduction process. At the low current densities the reduction potential plus over-voltage for uranium is less than the potential for water plus hydrogen over-voltage but, as current density increases, the over-voltage for uranium reduction probably increases more rapidly than that of the hydrogen over-voltage so that the reduction of water will become the principal reaction.

Thus it may be seen that cathode potential must be less than that represented by *A* in Fig. 13 in order that uranium reduction be the cathode reaction. Increased temperature tends to lower the over-voltage and therefore conditions must be adjusted so that the cathode current density or cathode potential is less than that of point *A*. On the other hand, increased pH increases the reduction potential of the water so that this curve is raised and, therefore, higher current densities and cathode potentials may be used. We have found that uranium is reduced at a copper cathode when the cathode potential is approximately −1 volt vs the saturated calomel electrode.

Other Recovery Processes

Uranium present in carbonate solutions as the uranyl tricarbonate complex may be recovered from solution by anion exchange resins. Workers at American Cyanamid Company, National Lead Company, and Dow Chemical Company have investigated this process.

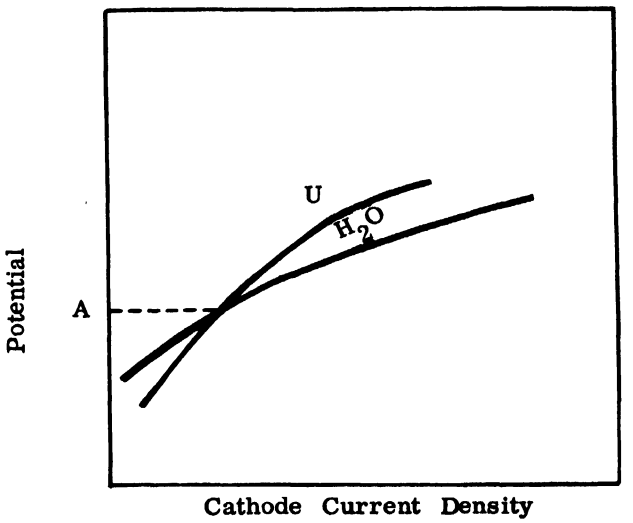

Figure 13. Reduction potentials of $[UO_2(CO_3)_3]^{-4}$ and H_2O

A solvent extraction system for the recovery of uranium from carbonate leach solutions is being developed in our laboratories at the present time.

Uranium recovered by precipitation of an insoluble salt of the uranyl tricarbonate complex has been investigated, but no practical precipitant has been found.

Discussion

The selection of any recovery process is of course dependent principally on the economics of the process considered in view of costs at the plant site. Preliminary estimates indicate that cost of the reduction processes and a combined lead vanadate and sodium uranate precipitation process are very favorable compared to the acidification method for recovery from vanadium bearing solutions. Estimates were not made for possible ion exchange or solvent extraction processes.

For recovery from solutions containing only uranium, all processes appear competitive. The reduction processes are more attractive than caustic precipitation however, since they yield a uranium oxide which is of higher grade than that obtained in the case of a uranate precipitate.

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Accelerated Thickening and Filtering of Uranium Leach Pulps

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The mechanical handling problem associated with separation of solids from liquids has markedly influenced the selection and development of uranium ore treatment processes. Pre-roasting of ores and use of common flocculating agents as starches and glues have been helpful for accelerating thickening and filtering of some ores but showed little benefit on others. Research was initiated early in 1953 at the Intermountain Experiment Station of the United States Bureau of Mines, Salt Lake City, Utah, to find better additives for improving thickening and filtration of uranium leach pulps and other plant products.

The work at Salt Lake City is continuing on reagent screening tests, fundamental aspects of flocculation and sedimentation, and development of techniques needed for commercial adaptation of the findings. This report presents first, a summary of the initial reagent screening tests; next, the results of tests illustrating the effects of the more important variables on application of specific reagents; and concludes with a summation of pertinent guides governing the effective employment of various additives for accelerating thickening and filtering.

Several hundred potential reagents including inorganic chemicals, reserve carbohydrates, gums, glues, starches and synthetic polymers were tested during the study. It is recognized that only a few potentially suitable reagents were tested and that some of those scanned did not appear to best advantage under the test conditions employed. Early dramatic success, however, was had with locust bean gum and then guar gum and cactus juice. Intensified industrial interest subsequently led to development of synthetic polymers which are as good or better flocculants than the natural products.

Reagents showing most promise in the screening tests were exhaustively tested on diverse ore types. It was found that guar gum, Separan, DF-381, and pear cactus extract were the most widely applicable of the reagents examined. As little as 0.05 to more than 1 pound per ton of a particular reagent was needed, according to circumstances. Use of these additives often improved the thickening rate fiftyfold and the filtration rate twenty-fivefold. Of the four reagents mentioned, only guar gum and Separan are commercially available. It is evident from the data later presented that the effectiveness of the flocculants depends on ore type, leach procedure, and reagent application technique. The selection of a flocculant for a specific application would necessitate comparative testing and economic evaluation.

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EXPLORATORY SCREENING TESTS

Exploratory flocculation tests were made by adding increasing quantities of the potential reagent to both acid and carbonate leach slurries of Lukachukai or Slick Rock ores at pH 1.0 and 10.2, and observing the improvement, if any, in the settling rate. Quantitative thickening tests using the classical method of Coe and Clevenger[1] subsequently were made on the more promising reagents. The outstandingly effective reagents under the conditions of the test are listed in Table 1.

In order to establish wide parameters of applicability for the more promising reagents, systematic testing was done on the following five Colorado Plateau ores of generally different handling characteristics: Slick Rock, Lukachukai, Temple Mountain, Utex, and White Canyon. The scope of the study was further extended to pulps from acid leaching the ores at both ambient temperature and 90°C, and carbonate leaching at 90°C. The leach procedures employed gave uranium extractions similar to commercial practice. The terminal pH at the end of acid leaching was 0.5 to 1.0. A solution containing 5 per cent $NaCO_3$ and 2 per cent $NaHCO_3$ used in the alkaline leach gave a terminal pH of 10.2.

All reagents except the cactus extract were made up as 0.5 per cent solutions. The gum solutions were made by slowly sifting the powder into vigorously agitated water at 80°C. After 15 minutes of agitation, 1 ml of 37 per cent formaldehyde was added per liter of solution as a preservative. The cactus extract was prepared by passing the prickly pear cactus nodes twice through a meat chopper then agitating 100 grams of the pulp in a liter of water for an hour. Suspended solids were filtered out and discarded.

Preliminary visual settling tests were made to determine the quantity of reagent necessary for maximum flocculation of the leach slurry. Subsequently, quantitative thickening and filtering tests were made with this reagent addition. The leach slurry in a 1-liter graduate was diluted to 25 per cent solids by

addition of pH 1.5 water or carbonate solution. The flocculant then was added and mixed with the pulp by inverting the cylinder three times. The thickener area was calculated from the single-zone settling rate. After settling at room temperature for 19 hours the supernatant liquor was decanted and the thickened pulp was filtered on an 18-cm Buchner using Reeves-Angle No. 202 paper under a vacuum of 16 to 18 inches of mercury. The time to dry-top for primary filtration plus two 75-ml displacement washes was a relative index of filterability.

The results of pertinent tests on Slick Rock ore are summarized in Table II. Except for minor variations, the other ores behaved in a similar manner. The typical thickening and filtering data given for Slick Rock ore demonstrate the advantages gained from use of aggregating agents. These and other tests, however, failed to show a costwise superiority for a specific reagent under all of the conditions investigated.

INFLUENCE OF SLURRY DILUTION ON EFFECTIVENESS ON FLOCCULANTS

Tests were made on both acid and carbonate leach slurries of Slick Rock ore at 50 per cent solids, and after dilution to 33 and 25 per cent solids, in order to observe the effect of slurry dilution on reagent performance. All leaches were at 50 per cent solids for 6 hours on 300-gram charges of ore dry-ground through 65 mesh. Sufficient acid was used in the ambient temperature leach to give a pH of 0.5 to 1.0. Solution assaying 5 per cent Na_2CO_3 and 2 per cent $NaHCO_3$ was used in carbonate leaching at 90°C.

The leach slurries were transferred to 1-liter graduates and diluted with pH 1.5 water or carbonate solution to the desired pulp density. Guar gum and Separan were added as 0.5 per cent solutions; the cactus as a 10 per cent solution based on weight of the original cactus nodes. The thickening and filtering test procedures were previously described.

Table I. Effective Aggregating Reagents for Acid and Alkaline Uranium Leach Slurries

Reagent	*Approximate price, dollars per pound*
American Cyanamid, S-3000	1.00
Cactus extract	Experimental
Dow Company, Separan	1.00
General Mills, Gum 39	0.22
Guar gum	0.35 to 0.40
Locust bean gum	0.35
Rohm and Haas DF-381	Experimental

The data in Table III shows that guar gum was relatively insensitive to changes in pulp density, whereas Separan and cactus extracts were much less effective in thick than in thin slurries. The tests with 0.2 pound of guar gum gave single-zone thickening rates of 0.8, 1.4, and 2.3 square feet per ton day as compared to 14.5, 15.1, and 6.3 square feet for comparable unflocculated acid slurries. Use of 0.2 pound of guar gum in the carbonate leach slurries improved thickening twenty to fortyfold and filtration threefold.

Although 0.1 pound Separan accelerates thickening and filtering of thin acid slurries, 0.4 pound per ton was barely adequate on a thick slurry. Cactus extract behaved similarly with twice the quantity being required for flocculation of a thick slurry. As on the acid slurries, larger quantities of both Separan and cactus extract were needed for effective flocculation of thick carbonate leach slurries.

No clear explanation is evident for the contrast in behavior of guar gum in thick slurries as compared to Separan and cactus extract. It might be postulated that these reagents are adsorbed and more firmly bound on the first particles encountered, thus precluding adequate dissemination of the reagent

Table II. Influence of Flocculants on Thickening and Filtering Slick Rock Leach Slurries. Preliminary Screening with Excess Reagent

	Flocculant		*Thickening data*		*Filtering data*	
Type of leach	*Name*	*Quantity, pound per ton*	*ft² per ton per day*	*Terminal density, per cent solids*	*Filter time, minutes*	*Filter cake, per cent solids*
Cold acid	None	—	12.1	41.3	20.0	71.9
	Cactus	16.7	0.4	59.4	21.0	81.7
	Hide glue	2.0	3.7	41.6	6.0	75.0
	Guar gum	0.5	0.9	59.3	3.7	75.8
	Separan	0.5	0.4	57.4	1.5	76.3
Hot acid	None	—	5.3	44.3	17.5	73.3
	Cactus	7.5	0.4	57.8	6.2	76.2
	Hide glue	1.0	2.6	47.5	7.6	70.1
	Guar gum	1.0	0.7	56.0	2.6	73.7
	Separan	0.5	0.4	53.7	0.8	77.7
Carbonate	None	—	20.8	45.4	6.2	75.0
	Cactus	8.3	0.4	59.8	1.2	75.3
	Hide glue	1.0	6.9	47.8	9.7	79.3
	Guar gum	1.0	0.5	60.2	0.4	76.2
	Separan	0.5	0.3	61.1	0.3	77.1

throughout the thick pulp. The effect of reagent dilution which bears on this same problem is taken up in the following section.

EFFECT OF REAGENT DILUTION ON BEHAVIOR OF FLOCCULANTS

The effect of flocculant dilution was studied on acid and carbonate leach slurries of Slick Rock ore. The customary 0.5 per cent solutions of guar gum and Separan, and 10 per cent solution of cactus were diluted to the requisite concentration with pH 1.5 water or carbonate solution. The diluted reagent then was used for final adjustment of the leach from 50 per cent to 33 or 25 per cent solids. Slurry and reagent were mixed by inverting the graduate three times.

There was no significant difference in the behavior of guar gum over the dilution range studied. Thickening and filtering rates were the same when using guar solutions of 0.5, 0.1, and 0.01 per cent strength.

Selected data given in Table IV for 25 per cent solids leach slurries show that both Separan and

Table III. Effect of Leach Slurry Dilution on Reagent Performance

Reagent	*Initial density, per cent solids*	*Initial settling rate ft per hr*	*Terminal density, per cent solids*	*Thickener area, ft² per ton day*	*Filtrate ml per minute*
Acid slurries					
No reagent	25	0.2	43.4	14.5	55
	33	0.1	47.2	15.1	45
	50	0.1	63.8	6.3	88
0.2 lb Guar gum	25	3.9	55.4	0.8	220
	33	1.2	55.7	1.4	110
	50	0.3	65.2	2.3	850
0.4 lb Guar gum	25	4.1	54.2	0.7	271
	33	2.3	55.4	0.7	235
	50	1.6	62.0	0.3	1140
0.2 lb Separan	25	2.9	54.8	1.0	142
	33	1.0	54.5	1.6	127
0.4 lb Separan	25	8.4	49.3	0.3	400
	33	3.5	53.6	0.5	244
	50	0.2	61.0	2.5	215
18 lb Cactus	25	3.1	51.7	0.9	150
	33	0.2	50.4	7.2	84
36 lb Cactus	25	99.0	57.8	<0.1	1400
	33	2.1	55.7	0.9	212
	50	0.3	60.8	2.1	205
Carbonate slurries					
No reagent	25	0.2	47.0	12.0	88
	33	0.1	49.4	10.8	77
	50	0.1	60.7	3.4	133
0.2 lb Guar gum	25	10.1	52.3	0.3	244
	33	2.9	53.6	0.5	238
	50	6.4	60.7	0.1	450
0.4 lb Guar gum	25	14.9	50.8	0.2	440
	33	5.1	54.8	0.3	390
	50	9.2	59.8	0.1	675
0.2 lb Separan	25	79.0	59.4	<0.1	650
	33	15.8	56.4	0.1	567
0.4 lb Separan	25	188.0	60.1	<0.1	1300
	50	0.9	64.0	0.6	275
18 lb Cactus	25	105.0	62.0	<0.1	1250
	33	22.9	59.3	<0.1	450
36 lb Cactus	25	317.0	58.6	<0.1	1350
	33	159.0	58.2	<0.1	1350
	50	12.8	62.0	<0.1	550

cactus extract reacted sharply to dilution. The test with 0.2 pound Separan showed thickening and filtering rates were not greatly different until a 0.005 per cent solution of the reagent was used. At this dilution, however, a tenfold increase in thickening and a fivefold increase in filtering rates were experienced.

Cactus extract similarly responded to dilution; 4 pounds of original cactus as 0.25 per cent solution was as effective as 18 pounds of a 10 per cent solution. The settling rate was increased tenfold, and the filtering rate was doubled by an 18-pound cactus addition as a 1 per cent solution rather than a 10 per cent solution.

Dilution affected the performance of Separan and cactus extract in carbonate slurries about the same as in acid pulps.

In order to benefit from dilution without introducing extraneous water, recycled pregnant solution was used to dilute the reagent. Pregnant solution from both acid and carbonate leaching proved satisfactory for dilution of slurry and reagents.

INFLUENCE OF SLURRY pH ON EFFECTIVENESS OF GUAR GUM AND SEPARAN

The effect of pH on flocculation with guar gum and Separan was examined by adjusting the pH of acid and carbonate leach slurries with Na_2CO_3 or H_2SO_4 as required. Leach slurries from 300-gram charges of minus 65-mesh Slick Rock ore were diluted to 33 per cent solids with pH 1.5 water or carbonate solution prior to adjusting the pH and adding the flocculant as a 0.5 per cent solution. The maximum permissible pH for acid slurries was about 3.0 and for carbonate slurries 10.6 as higher pH caused precipitation and vitiated the test data.

Both guar gum and Separan were shown to be better in alkaline than in acid slurries. However, the results in Table V do not otherwise indicate that pH has marked influence on the performance of the reagents within the ranges studied.

OBSERVATIONS AND GUIDES ON USE OF FLOCCULANTS

The data and observations from the research showed that several factors have a pronounced effect on flocculants for accelerated thickening and filtration of uranium leach pulps. The more pertinent factors encountered in testing and applying flocculants are reviewed briefly.

Reagents Storage and Preparation

No particular storage or solution preparation problems were encountered when using the synthetic polymers. The vegetable gums, however, must be kept dry in storage and care taken in preparing the water sols to insure a smooth lump-free reagent. The 0.5 per cent gum solutions which are convenient for laboratory work are readily prepared by sifting 5 grams of the powdered gum slowly into a liter of vigorously agitated water while heating at 80°C. Only a few minutes are needed for feeding the powder, and agitation then is continued for about 15 minutes without heating. A preservative such as formaldehyde is added to inhibit bacterial decay. Natural gum and glue solutions prepared in this manner showed no noticeable deterioration after standing for several days at room temperature.

The gums can be dissolved by extended vigorous agitation in cold water. Addition of a small quantity of borax facilitates solution of the gums. The borax also appears beneficial as the floccules are more resistant to degradation during handling.

Addition of Flocculant

The method of adding the flocculant to the pulp appears to be the most important factor governing effectiveness of the reagent. The crux of the problem is to disseminate the flocculant uniformly throughout the slurry without deforming the floccules. Intense agitation to distribute the reagent for maximum effectiveness degrades the fragile floccules and thus defeats its own purpose. Data from several ores show that flocculant requirements increase with intensity and time of agitation.

Flocculation of relatively dilute pulps is much easier than for thick slurries. Determination of what constitutes a dilute slurry is complicated by the fact that the nature of the solid component has a pronounced influence on slurry handling; slime pulps containing only 10 per cent solids may present unusual handling difficulties, whereas other pulps may be readily flocculated at 50 per cent solids. When making tests on dilute pulps in graduated cylinders, satisfactory mixing of the reagent and pulp can be obtained by inverting the cylinder three or four times. When testing thicker slurries, reproducible results can be obtained by simultaneously pouring the slurry and reagent into a container and then further blending by pouring the mixture back and forth into a second container three or four times. Stage addition of the reagent frequently was beneficial.

Reagent Quantity

The optimum quantity of flocculant for a specific application is affected by a host of technical and economic factors. In general, smaller quantities are needed for accelerating thickening than for filtering. The larger quantity required for filtering may be due to lack of dissemination of the reagent throughout the thick pulp. Reagent additions for thickening may be deleterious in subsequent filtration of the thickened mud. In such instances additional reagent is necessary for accelerating filtration.

The intensity of flocculation and the speed of settling can be varied within wide limits by regulating the reagent quantity. The increase in thickening rate with guar gum is almost linear until a plateau is reached and then regresses upon further addition. The plateau may be reached with as little as 0.8 or as much as 20 pounds per ton of solids, depending upon the slime content of the slurry. Flocculation of primary ore slimes and chemical precipitates may

Table IV. Effect of Reagent Dilution on Performance of Separan and Cactus Extract

Reagent	Reagent solution strength, per cent	Initial settling rate, ft per hr	Terminal density, per cent solids	Thickener area, ft^2 per ton day	Filtrate ml per minute
Acid slurry					
No reagent		0.2	43.4	14.5	55
0.2 lb Separan	0.5	2.9	54.8	1.0	142
	0.1	1.7	50.8	1.5	220
	0.05	1.6	49.6	1.6	180
	0.01	3.5	50.5	0.8	150
	0.005	19.0	54.5	0.1	925
18 lb Cactus	10.0	3.1	51.7	0.9	150
	2.0	8.8	57.9	0.3	258
	1.0	41.0	62.4	<0.1	287
4 lb Cactus	0.25	2.2	55.0	1.3	138
9 lb Cactus	0.1	23.7	56.4	0.1	235
Carbonate slurry					
No reagent		0.2	47.0	12.0	88
0.2 lb Separan	0.5	79.0	59.4	<0.1	650
	0.1	151.0	60.0	<0.1	1500
	0.05	178.0	60.1	<0.1	1500
	0.01	227.0	59.2	<0.1	1500
18 lb Cactus	10.0	105.0	62.0	<0.1	1250
	2.0	240.0	59.2	<0.1	1250
	1.0	200.0	59.5	<0.1	1250
4 lb Cactus	0.25	9.8	57.0	0.3	160
9 lb Cactus	0.1	97.0	61.0	<0.1	1250

require inordinately large quantities of reagent. The plateau and regression observed for guar and similar natural gums were not observed when using Separan or cactus extract.

When handling pulps by multiple-stage countercurrent decantation, or by filtration and repulping, supplemental additions of reagent generally are needed ahead of each stage. The quantity needed is related to degradation of the glomerules when mixing with the advancing wash solution. In pilot plant work at Salt Lake City, using Esperanza classifiers as thickeners for countercurrent washing of intensely flocculated pulps, it was necessary to install small mixers with slow-moving propellers for blending the thickened pulp and advancing wash water. The supplemental reagent was added to the overflow of the mixer before advancing to the next classifier. Proper addition of a small quantity of reagent gives better flocculation than an improperly added larger quantity.

Reagent Dilution

Use of dilute solutions of Separan and cactus extract in particular greatly increases the effectiveness of these reagents. In order to avoid difficulties in subsequent processing owing to excessive dilution, use of recycled pregnant solution as a reagent diluent seems indicated. Dilution of the reagent with pregnant liquor from either acid or carbonate processes was not detrimental to performance of the reagent. The potentially large benefits possible from increased reagent dilution may more than compensate for a higher solution inventory. Since filtration rates generally drop off with increasing pulp dilution, the advantages of highly diluted reagents as an aid in filtering may be limited.

Slurry dilution is so closely related to reagent dilution that both must be considered together. Although it would seem that diluting the slurry should give the same over-all effect as diluting the reagent, indications are that dilution of the reagent is the more beneficial.

Physical and Chemical Nature of the Solids

The particle size of the solids plays a critical role in the use of additives for accelerating thickening and filtering. Quantitative data are incomplete, but there are indications that the chemical nature of the solids has an important effect on reagent performance. Primary ore slime in the submicron range and amorphous chemical precipitates, owing to the enormous surfaces presented, are avid consumers of reagents. Presence of large quantities of slime, even

Table V. Influence of Slurry pH on Performance of Guar Gum and Separan

Reagent	Slurry pH	Initial settling rate, ft per hr	Terminal density, per cent solids	Thickener area, ft² per ton day	Filtrate ml per minute
Acid slurry					
No reagent	1.0	0.1	47.2	15.1	45
0.6 lb Guar gum	1.0	2.4	51.6	0.6	525
	2.0	5.8	54.0	0.3	900
0.6 lb Separan	1.0	10.7	55.9	0.1	1000
	2.1	8.8	57.7	0.2	725
	2.9	9.9	49.6	0.2	717
Carbonate slurry					
No reagent	10.2	0.1	49.4	10.8	77
0.6 lb Guar gum	10.2	12.2	55.4	0.1	583
	9.0	9.4	54.7	0.2	600
	8.0	7.4	53.7	0.2	500
	7.1	9.0	55.3	0.2	172
0.6 lb Separan	10.2	51.2	58.8	<0.1	1400
	9.0	98.6	58.8	<0.1	1400
	8.1	81.5	59.1	<0.1	1400
	6.8	33.5	58.0	<0.1	1400

in relatively dilute slurries, complicates the problem of adequately disseminating the reagent for effective use.

Single-zone settling tests on slime materials are likely to be misleading. Differences in the deportment of slime pulps are so pronounced that generalizations regarding their treatment are difficult. In some instances, large reagent additions were ineffective for either thickening or filtering. In others, moderate additions improved thickening without effect on filtering, or the converse also was true. Sometimes only a specific reagent is effective as illustrated by the efficiency of small quantities of Separan in settling slimes from phosphoric acid liquor.

Composition of the Pregnant Liquor

Not too much is known about the effect of cations and anions in the pregnant liquor on the performance of flocculants. In at least one instance, however, the response to guar gum was improved markedly when molybdenum and copper were precipitated before addition of the flocculant.

Clarity of Pregnant Solutions

Supernatant liquors and filtrates produced by thickening and filtering when using additives are not always sparkling clear. There is some indication that the synthetic polymers and natural gums are selective for specific minerals and do not flocculate others. Specific particle sizes also may resist flocculation. It has been possible to select a specific reagent which will produce clear liquors in a certain application. Clarity generally can be improved by using a small amount of gelatin or glue in conjunction with the primary flocculant. Addition of as little as 0.05 pound of glue or gelatin per ton of solids proved adequate. On some leach slurries the order of reagent addition is critical, whereas on others the reagents can be added together. It generally follows that clarity of the liquor can be improved by some sacrifice in thickening rate.

The interaction of certain polyelectrolytes on the flocculation of mineral colloids was studied by Wadsworth and Cutler.[2] In this connection our tests have shown that a combination of guar gum and Separan was more effective than costwise equivalent quantities of either reagent alone.

Washing of Thickener Underflows and Filter Cakes

Washing of thickener underflows and filter cakes previously was mentioned. Although good displacement washing was obtained in the laboratory batch tests, effective washing in continuous practice generally required repulping. The full possibilities of displacement washing of heavily flocculated filter cakes remain to be explored.

Thickening and Filtration Equipment

Pilot plant and commercial thickening of leach slurries have shown that thickener requirements cannot be accurately predicted from small-scale static settling tests. Actual requirements generally are severalfold greater than indicated by the laboratory data. More precise experimental methods that can be realistically extrapolated to plant operation need to be developed. The work of Talmage and Fitch[3] may be a notable advance in measuring thickening area requirements.

Laboratory filtration tests using a Buchner funnel, although suitable for comparing the relative effectiveness of reagents and examining pertinent variables, give rates that can be duplicated only on a horizontal pan-type filter. Laboratory testing with a filter leaf in which the cake is picked up by suction gives more valid results for extrapolating to drum or disk filters. The full potential of flocculants cannot be realized when using drum or disk filters because the heavily flocculated pulp has a slippery texture and does not adhere well to the filter. Consequently, it is necessary in continuous filtration to reduce the reagent quantity and rotate the drum or disk faster in order to pick up a thinner and more adherent cake. Although various types of filter media have been tested in the laboratory and pilot plant, no definite preference has been established to date.

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A General Survey of Types and Characteristics of Ion Exchange Resins Used in Uranium Recovery

By Albert Preuss and Robert Kunin,* USA

The exhaustion of high grade uranium deposits necessitated the development of new hydrometallurgical techniques for the recovery of uranium from low grade ores. The relatively new field of ion exchange is important in the success of these processes.

At first, various investigators throughout the United States studied the use of cation exchange resins for uranium recovery because uranium was thought to exist in solution solely as the uranyl cation. In early 1949, workers at the Rohm & Haas Company found that uranyl ion could be complexed to form anions which were selectively adsorbed on Amberlite IRA-400, a strongly basic anion exchange resin which had just been developed commercially. Subsequent studies proved the utility of this resin for the upgrading and purification of uranium in sulfuric acid and sodium carbonate leach solutions.

The columnar ion exchange process now in use consists of the following:

1. The clarified leach liquor is passed through a column of resin at a moderate flow rate until the presence of uranium is detected in the effluent.
2. The column is rinsed and backwashed with water.
3. The uranium is eluted (desorbed) with a chloride or nitrate salt solution at a flow rate considerably lower than the adsorption flow rate.
4. The uranium is precipitated from the eluate with ammonia or some other alkaline agent and the precipitate is filtered, dried and calcined.

The above ion exchange operation has been in use in various places on a commercial basis and the results have indicated that at least 98 per cent of the uranium in the leach liquor can be recovered as a concentrate having a U_3O_8 content greater than 80 per cent.

The "Resin-In-Pulp (RIP)" process differs from the columnar operation only in that the resin is held in screened baskets which allows unfiltered pulps to pass freely through the resin bed. This permits uranium recovery from ore slurries which are very difficult to filter or thicken.

The selection of an ion exchange resin involves a study of their general chemical and physical properties such as exchange capacity, hydration, density, hydraulic characteristics, rates of exchange, selectivity for uranium, and life expectancy.

NATURE OF THE URANIUM ION IN SULFURIC ACID AND SODIUM CARBONATE SOLUTIONS

Sexivalent uranium is complexed by sulfate ion in sulfuric acid solutions. The equilibrium may be written as

$$UO_2^{++} + nSO_4^{=} \rightleftarrows UO_2(SO_4)_n^{2-2n} \qquad (1)$$

where $n = 1, 2,$ or 3.

The formation constants[1] for these complexes are

$$\begin{array}{ll} n = 1 & K_1 = 50 \\ n = 2 & K_2 = 350 \\ n = 3 & K_3 = 2500 \end{array} \qquad (2)$$

In carbonate solutions, the complex is much stronger and the equilibrium may be written as,

$$UO_2^{++} + 3CO_3^{=} \rightleftarrows UO_2(CO_3)_3^{4=} \qquad (3)$$

The fact that sexivalent uranium exists as strongly anionic complexes in both carbonate and sulfuric acid solutions enables one to employ anion exchange resins in both sulfuric acid and carbonate leach liquors, the two major leach systems.

TYPES OF ION EXCHANGE RESINS USED IN URANIUM RECOVERY

Sulfuric Acid Solutions

Inspection of the equilibrium constants for the sulfuric acid solution shows that uranium(VI) may exist both as the cationic uranyl ion or as the anionic sulfato complex depending on the uranium and sulfate concentrations. It should then be possible to adsorb uranium on ion exchange resins, either as a cation or as an anion and this has been found to be true. If one considers what ionic species would be present in a typical sulfuric acid leach solution, the most important ones would be:

Cations	*Anions*	
UO_2^{++}	$UO_2(SO_4)_n^{2-2n}$	$n = 2, 3$
Fe^{+++}		
Fe^{++}	$Fe(SO_4)_n^{3-2n}$	$n = 2, 3$
Al^{+++}		
Mn^{++}	$SO_4^{=}$	
Mg^{++}		
Ca^{++}	HSO_4^{-}	
H^{+}		
Na^{+}		

It is therefore readily seen why attempts to adsorb uranium as the uranyl ion on cation exchange resins

* Rohm & Haas Company, Philadelphia, Pennsylvania. Including work by Sallie Fisher, Charles Dickert, Francis McCarvey and Jean Saunders.

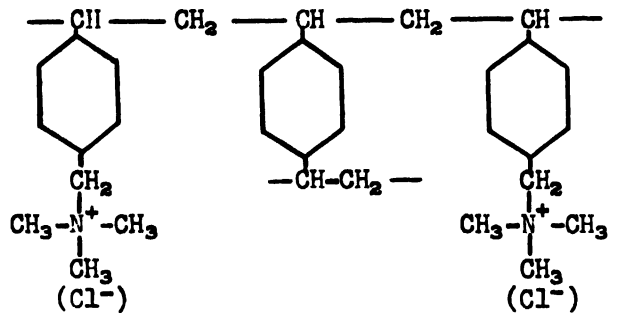

Figure 1. Structure of a quaternary ammonium anion exchange resin

are possible but not worthwhile since ferric, aluminum, and other ions are also adsorbed along with the uranium.

Anion exchange resins, particularly those with quaternary ammonium functional groups, were found to be selective for uranium over sulfate, bisulfate, and iron(III) sulfate complexes. Only resins of this type are currently used for uranium recovery from acidic sulfate solutions. Resins with weak base functional groups also adsorb uranium but their capacity and selectivity are not as great as the quaternary types.

Sodium Carbonate Solutions

The equilibria in carbonate solutions are such that the anionic complexes predominate. Only quaternary ammonium type anion exchange resins may be used since weak base resins have but little activity generally in alkaline solutions.

GENERAL CHARACTERISTICS OF ION EXCHANGE RESINS

Ion exchange resins are water-insoluble crosslinked polyelectrolytes of high molecular weight. The resins consist of crosslinked polymers in which ionic functional groups have been introduced.

Structure of a Quaternary Ammonium Exchange Resin

Typical of the resins used in uranium recovery processes is the product obtained by amination of a chloromethylated styrene-divinylbenzene copolymer with trimethylamine (Fig. 1).

This is in contrast to the amination with primary, secondary, or polyamines which leads to weak base resins and the direct sulfonation of the styrene-divinylbenzene copolymer to produce a strongly acidic cation exchange resin with a nuclear sulfonic functional group.

Exchange Capacity

Ion exchange resins are rated by their exchange capacity. The number of fixed ion sites on the resin can be ascertained by measuring the number of mobile ions which may be adsorbed and desorbed from a given weight or volume of resin.

Capacity measurements are normally reported both on a dry weight basis and on a volume basis. Since the capacity per unit volume determines the size of the ion exchange equipment, this measurement is considered to be the more important of the two. Resins used in uranium recovery processes have total exchange capacities ranging from 3.0 to 5.0 milliequivalents per dry gram and from 1.0 to 1.8 milliequivalents per milliliter of wet settled resin.

Hydration

All ion exchange resins are hydrophilic because of the presence of the fixed ion groups. Although the fixed ions groups themselves may not be hydrated[2] because of steric effects, the mobile or counter ions are hydrated to approximately the same degree as are free ions in solution under comparable conditions. Therefore the hydration of the resin is a function of its exchange capacity and its counter ion as well as the nature of its functional group and the type of crosslinked polymer backbone. The equilibrium moisture of the resins used in uranium recovery are in the range of from 40–60 per cent.

Particle Size

In columnar operations, the particle sizes of the resin are such that exchange may take place in a reasonable length of time, solution flow may be maintained with a minimum of pressure drop, and the resin beds may be cleaned through a backwash step. In columnar operation, the majority of the resin beads are in the particle size range of 0.3 millimeters to 0.9 millimeters in diameter. This size range is a compromise of exchange rates, capacities, and hydraulic characteristics of the resin.

For the "Resin-In-Pulp" operation, wherein the resin bed is held by a screen, the beads are larger in order to effect a slime-resin bead separation. These tailor-made beads range principally between 0.8-1.6 millimeters in diameter.

Density

The prime density requirement for an ion exchange resin is that its true density be greater than that of the medium in which it is used. Its apparent density is defined as that weight of backwashed and settled wet resin which will occupy one cubic foot of space. The apparent density is related to the true density by the relationship

$$\text{apparent density} = \text{true density} \; (1 - \text{fraction of void space}) \qquad (4)$$

The void space for uniform spheres approaches approximately 40% of the total volume. The apparent densities of ion exchange resins used in uranium recovery vary from 38 to 45 pounds per cubic foot.

Attrition and Solubility Losses

Attrition losses in ion exchange resins may be due to the swelling and contraction of the resin, abrasion of resin-resin surfaces, and abrasion of resin-equipment surfaces. Abrasion losses in column operations are insignificant. Losses due to swelling and con-

traction of certain resins may be large but volume changes in normal operations are less than 10 per cent. Losses due to attrition have not been found to any extent in column operations in the uranium recovery program.

However, the "RIP" process which requires larger beads and constant agitation has presented some initial loss in resin due to attrition. However, these losses have been minor and are not great enough to present any major problems.

Solubility losses are so small that solubility measurements cannot be made.

Hydraulic Characteristics

The hydraulic characteristics of resins are analogous to any inert spherical particles. Factors which affect good column operation are temperature, particle size, density and compressibility.

Pressure drop, the loss in head per foot of resin depth, is very low with the resins used in uranium recovery. Pressure drops of the order of one pound per square inch per foot of resin depth are obtained with clean resin beds. When slime formation and precipitation occur in the resin bed, pressure drops increase. In addition, non-uniform flow or channeling occurs.

To prevent these occurrences, the resin beds are backwashed at convenient times, either at the end of the adsorption cycle or at the end of the desorption cycle. Backwashing is the upflow operation which allows the resin particles to be expanded so that fine, extraneous matter may be removed from the ion exchange column. Ion exchange columns are usually designed to allow room for 100 per cent expansion of the resin bed during backwashing. The flow rate necessary to attain maximum expansion is dependent on the viscosity of the backwash fluid, the particle size of the resin, and the true density of the resin.

Rates of Exchange

The rate determining step in the ion exchange process is the diffusion of the ions into the resin matrix so that it may be adsorbed on the fixed ion sites. To allow for this, retention times for uranium adsorption vary from 2 to 10 minutes. The retention times used are those which allow nearly full equilibrium to be attained.

Selectivity

The selectivity for the quaternary ammonium ion over the iron(III) sulfate complex, sulfate ion and bisulfate ions is high. Adsorption from most uranium leach solutions leaves the resin sites almost completely occupied by the uranyl(VI) sulfate complex. Some iron is adsorbed but this is removed readily so that the final uranium solution obtained by elution of the resin column is quite pure. Direct precipitation of this eluate results in a high grade uranium cake containing more than 80% U_3O_8. Where much iron is present in these eluates its separation can be effected by careful pH control.

Life Expectancy

The life of a resin in uranium recovery will depend on the leach solution with which it is used. With clean, clarified leach liquors containing as anions only uranium, iron, sulfate and bisulfate ions the resins need not be replaced before at least two years' time. In other cases where, by the nature of the ore, the solutions contain ions which are permanently adsorbed on the resin shorter resin lives are realized. Other ions which cause reactions to take place which are detrimental to the functional group also decrease the resin life.

Although the initial cost of the resin may appear expensive relative to other chemicals, its repeated use over long periods of time reduces the cost to a minor fraction of the total plant expenditures.

OPERATING CHARACTERISTICS OF ION EXCHANGE RESINS IN URANIUM RECOVERY

Adsorption Cycle

The loading or adsorption cycle requires a high capacity resin which will adsorb uranium completely from a leach solution at reasonable flow rates.

Curve *A* of Fig. 2 is a characteristic adsorption curve for the loading of uranium on Amberlite IRA-400. Curve *A* is the curve obtained under the optimum conditions. Curve *B* shows deviations which are caused by interdependent factors. Curves of type *B* are obtained when one or more of the following conditions exist:

1. The flow rate is too high or the retention time is too short for equilibrium to be obtained.
2. The particle size of the resin is too large.
3. The resin is not selective for uranium over other anions in solution.
4. The resin is too dense to permit ion exchange equilibria to be attained in a reasonable time.

The positions of points *a* and *b* are important because they determine the amount of uranium which can be adsorbed per cycle.

Rinse Cycle

The rinse or displacement cycle removes leach liquor which occupies the void space between the resin particles.

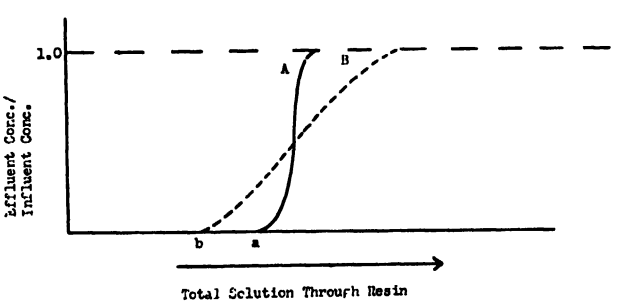

Figure 2

Backwash Cycle

After rinsing, the resin is backwashed to remove the extraneous matter which has accumulated during the load cycle.

Elution Cycle

After the uranium is adsorbed, and the column rinsed and backwashed, the resin is then eluted. This is done with the preferential adsorption of other ions such as nitrate or chloride ions which, when present in large concentrations, replace the uranium ions. This solution or eluate is passed through the resin at a retention time severalfold that used during the adsorption cycle.

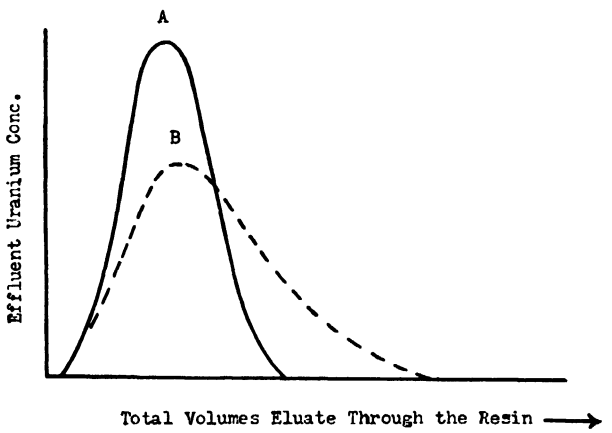

Figure 3

Curve *A* of Fig. 3 is the characteristic elution curve for the desorption of uranium from Amberlite IRA–400 under optimum conditions. Curve *B* shows deviations from the optimum which are caused by the same interdependent factors which affected the loading curve of Fig. 2. These are: (1) too small retention time; (2) too large particles; (3) the resin is not selective for the eluting ion; and (4) the resin is too dense.

Rinse after Elution

After elution the resin sites are all occupied by the eluting ion. To displace the solution in the void space, a short water rinse is made. At this stage there sometimes are precipitates which formed during the elution cycle. Wherever necessary, the resin may be backwashed at this point in the operation.

Reloading

After the rinse, the ion exchange column is ready for the next loading cycle. The ions which were adsorbed to replace the uranium are removed by the first few volumes of leach liquor which passes through the resin.

SUMMARY

The recovery of uranium from low grade ores has been facilitated by use of ion exchange processes. By use of these techniques it is possible to produce a high grade uranium precipitate assaying greater than 80 per cent U_3O_8.

Of the commercially available anion exchange resins only those of the quaternary ammonium type such as Amberlite IRA–400 have been found to be of practical importance in uranium recovery. The properties of these resins which were studied were exchange capacities, hydration, particle size, rates of exchange, selectivity, hydraulic characteristics and life expectancy.

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Recovery of Uranium from Sulfuric Acid and Carbonate Leach Liquors by Anion Exchange

By Robert R. Grinstead, David A. Ellis, and Robert S. Olson,* USA

The uranium milling industry is primarily a hydrometallurgical operation. Processes fall into one of two categories: the acid-leach and the carbonate-leach processes. The subsequent treatment of both types of clarified leach solutions has been accomplished in the past by chemical methods which were both complicated and expensive. Although improvements in chemical methods since World War II have resulted in some savings, the application of the newer techniques such as ion exchange and solvent extraction has given promise of still greater reductions in processing costs.

Ion exchange processes have been developed in this laboratory for the recovery of uranium from clarified leach solutions of both the acid and carbonate processes. Parallel development of the ion exchange process for acid leaches has been carried on at other laboratories, particularly the US AEC Raw Materials Laboratory at Winchester, Massachusetts,† and the process is actually in commercial operation at a number of places. The Winchester group has developed the method further by treating desanded leach pulp with resin contained in mesh baskets. The clarification problem has always been a real one, and the potential savings to be derived by omitting it are in some cases quite large. However, due to recent improvements in thickening and filtration techniques, these costs have decreased somewhat and it is likely that they may be reduced still further.

Since very little work has been done at this laboratory on the actual ore handling and leaching methods, this paper will be confined to the treatment of the filtered leach solutions by the methods of columnar ion exchange. Because the chemistry of the acid and carbonate processes differs in many respects, each process will be taken up separately.

SULFURIC ACID ION EXCHANGE PROCESS

Process Description

In Fig. 1 is shown a block diagram of the sulfuric acid ion exchange process. Conventional crushing and grinding steps are used. On the Colorado Plateau, the ores are reduced to 10 or 20 mesh during this step. Almost without exception sulfuric acid is used to leach the ore, although at one mill some by-product HCl from vanadium operations is used to augment this.

The leaching and clarification steps are handled in various ways: in some places by percolation leaching, and in others by agitation, thickening, and filtration. Whatever the method, a clear liquor is required at this point to prevent plugging of the resin beds.

Three or four resin beds are utilized in this process. Leach solution flows through two or three in series while the remaining bed is being regenerated. Uranium is sorbed by the resin; and when uranium is detected in the final effluent, the freshly regenerated bed is switched in downstream to act as a "cleanup" bed. The upstream bed is switched out and regenerated preparatory to use as the "cleanup" bed when the next switch point occurs. This type of operation has been termed "merry-go-round" operation because of its cyclic character. The beds consist of strong-base quaternary amine anion resins which have a strong affinity for the uranium species. Recoveries of greater than 99% are not difficult to achieve, and resin loadings are usually in the range of 30–100 grams U_3O_8/liter of wet-settled resin. The resin bed is converted to the sulfate form during the sorption step.

Elution may be effectively accomplished with either 1 *M* chloride or 1 *M* nitrate solutions, containing about 0.1 *M* concentration of the corresponding acid. The eluate which is drawn from the bed is neutralized with a base to precipitate uranium, filtered, and recycled to the eluant circuit where it is reacidified. Actually, a portion of this solution must be discarded to prevent excessive buildup of sulfate, and this point will be discussed below. The uranium precipitate is washed and dried.

Sorption of Uranium

In sulfate and sulfuric acid solutions uranium exists partly in the form of anionic complexes. During passage through an anion resin bed the following type of reaction occurs: (where *R* denotes the resin matrix)

$$4RCl + [UO_2(SO_4)_3]^{4-} \rightarrow R_4[UO_2(SO_4)_3] + 4RCl^- \qquad (1)$$

Recent work at the USAEC Raw Materials Laboratory has shown that both the di- and tri-sulfate

* The Dow Chemical Company, Pittsburg, California.

† Operated by the National Lead Company (formerly operated by the American Cyanamid Company).

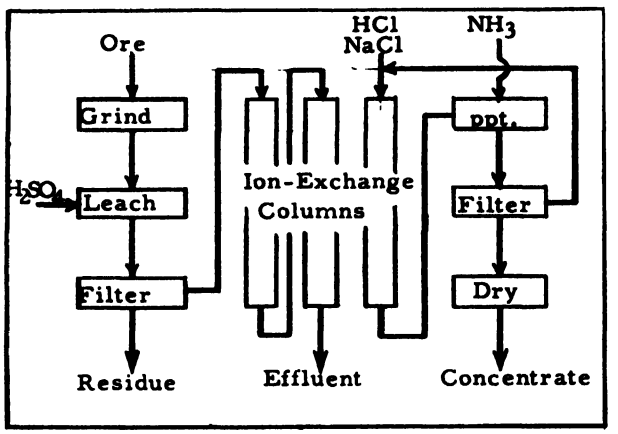

Figure 1. Block diagram of ion exchange process for sulfate solutions

complexes are present on the resin. In order for sorption to occur the presence of some sulfate is, of course, necessary. In the absence of interfering ions the sorption proceeds very effectively with sulfate concentrations of only a few grams/liter. In practice the acid requirements for leaching are usually sufficient to insure the presence of at least 10–20 grams $SO_4^=$/liter, which is a great excess. Some competition for the resin by the uranium complex and free sulfate occurs, but this is not serious.

The distribution of uranium between resin and solution depends upon several factors. These factors can be grouped into one of two general headings, e.g., the composition of the solution and the type of resin. Because of space limitations, the discussion of these factors will be of a general nature, but will be supplemented as much as possible by specific data. The behavior of a wide variety of sulfate solutions has been examined in this laboratory, including those obtained from high-grade Canadian ores, from the South African Rand gold residues, and from the phosphate industry. Principal emphasis has been placed on Colorado Plateau leach solutions. Most of the discussion will concern data obtained from these solutions, but data obtained from other systems will be mentioned. The range of concentrations in this type of solution is given in the following table.

Constituent	*Range of concs., gm/l*
U_3O_8	0.4–4
V_2O_5	0–5
Al	0.5–5
Fe	1–5
$SO_4^=$	20–80
PO_4^{---}	0–10
Cl^-	0–25
pH	0.5–1.5

Uranium and vanadium are usually found in the (VI) and (IV) oxidation states, respectively, while iron occurs as a mixture of the (II) and (III) states.

The resin used in the majority of the work was a −50 + 100 mesh Dowex 1, a quaternary amine resin with a styrene-divinylbenzene matrix. Although commercial resins are usually in the range 20 to 40 mesh, the finer size was favored because better performance was obtained both in total uranium capacity and in exchange rates. Pressure drops are higher but still within the practical range of plant equipment. More weakly basic resins will sorb uranium as well as, or better than, the quaternary amine resins but the former are difficult to elute and are therefore not satisfactory.

When a leach solution is passed through a resin bed, the effluent is initially nearly free of uranium. The uranium level gradually builds up and finally reaches the level of the influent. At this point the resin is in equilibrium with the solution, and is said to be "loaded." A plot of the effluent uranium concentration against effluent volume is known as a breakthrough or sorption curve. A typical curve

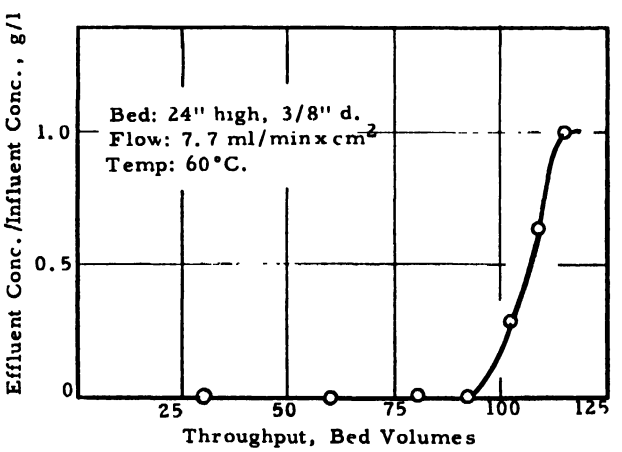

Figure 2. Breakthrough curve, Marysvale leach

is shown in Fig. 2. The solution used was a sulfuric acid leach of an ore from the Marysvale, Utah, district. As with other systems involving packed beds, the steepness of the curved portion increases when: (1) the flow rate decreases, (2) the bed depth increases, (3) the resin bead size decreases, or (4) the temperature increases. Temperature effects are not usually large and there is usually sufficient flexibility in other variables to take care of temperature variations. The other three variables are mechanical in nature and do not affect the equilibrium resin loading of uranium. Because they are interrelated, selection of the proper combination of conditions is required in order to achieve efficient operation of a merry-go-round unit.

One of the most critical variables affecting the distribution coefficient or uranium, Kr/a (grams U_3O_8/liter of wet-settled resin/grams U_3O_8/liter of solution), is the solution pH. In Fig. 3 is shown the effect of pH upon Kr/a for a sulfuric acid leach of a Plateau ore containing about 3 grams U_3O_8/liter. Raising the pH from 0.5 to 1.5 increases Kr/a nearly threefold. This effect is attributed to an increase in the sulfate concentration at the expense of bisulfate as the pH is raised. The increased sulfate concentration causes a higher percentage of the ura-

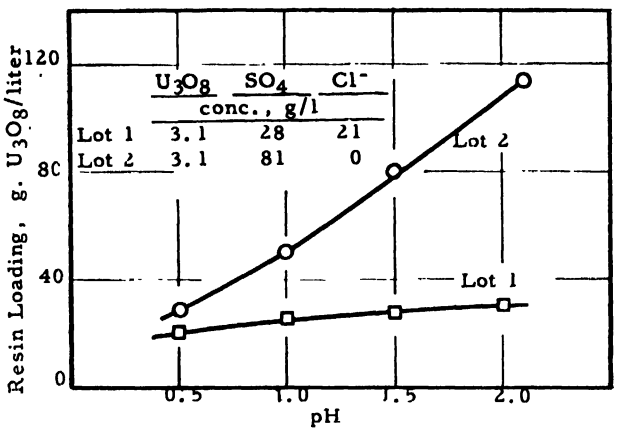

Figure 3. Effect of pH on resin loading

nium to exist in the form of the sorbable anionic complexes.

In this range of uranium concentrations the distribution curves are concave toward the solution axis, with the result that, as the uranium content of the solution decreases, the coefficient increases. For example, the *Kr/a* value for a Marysvale ore leach containing 0.4 grams U_3O_8/liter was 85 at pH 1.0 compared to 17 for the leach shown in Fig. 3 (3 grams U_3O_8/liter) at the same pH.

The sorption of uranium is also affected by the presence of certain other chemical species in the leach. A cumulative effect is observed due to buildup on the resin of certain trace components known as "poisons." This phenomenon will be discussed in a subsequent section. Adverse effects may also be due to species which affect the equilibria in solution. The most important of these species are chloride and nitrate. At one plant ore is roasted with NaCl to solubilize vanadium, and the resulting leach solution contains variable amounts of chloride. The effect of chloride is shown qualitatively in Fig. 3. The Lot 1 solution contained 21 grams Cl^-/liter, and the loading in the pH range 1–2 was only 30–50% of that from Lot 2. Lot 1 contained only one-third as much sulfate as Lot 2. However, the effect of sulfate is to compete with the uranium complex so that had the two solutions contained equal sulfate concentrations the difference in resin loading would have been even greater than was observed.

Nitrate has an equal or greater effect but is encountered less often. It is known that chloride and nitrate have a strong affinity for the uranyl ion; the effect of these anions in moderate concentration is evidently due to the formation of cationic and neutral complexes. In the presence of these complexes the concentration of the sorbable anionic species is reduced, and the resin loading is correspondingly decreased.

Phosphate is not ordinarily found in this type of solution, but considerable amounts can be tolerated. Only a small fraction of the phosphate in solution is sorbed by the resin, some of it probably as a uranyl-phosphate complex. However, the amount of phosphate on the resin is appreciable when compared to the uranium and will contaminate the product. Ferric iron is sorbed by the resin to a slight extent but does not usually give serious trouble. In solutions such as those from South African operations, where the concentrations will be of the order of 0.5 gram U_3O_8/liter and 3–4 grams Fe/liter, iron may occupy several per cent of the capacity of the loaded resin. The chief difficulty in this situation is that the product will then contain 10–20% iron by weight.

Vanadium(IV), aluminum, manganese, ferrous iron, alkali and alkaline earth metals are not picked up from sulfate solutions by anion resins. Vanadium (V) is sorbed, but this is easily prevented by reduction to the (IV) state with SO_2 or $FeSO_4$. Several of the less commonly encountered metals are also rejected, such as copper, cobalt, nickel and rare earths. Arsenate is sorbed to some extent, since it is an anion, and it is carried through into the uranium concentrate.

Elution

In theory, elution can be accomplished by using any ionic salt, in which case replacement of the uranium species should occur by simple ion exchange. Because the complex favors the resin so strongly, the eluant must also possess other characteristics. The most effective eluants have been found to be nitrate and chloride solutions, which act through a complexing mechanism described above. Neutral nitrates or chlorides are fairly effective as eluants but their efficiency is raised considerably by acidification. This is to be expected in view of the direction of the pH effect on sorption. Moderately strong sulfuric acid is a reasonably good eluant, probably because the free sulfate concentration is low. The difficulty of subsequent treatment precludes wider use of this reagent. The optimum composition of chloride or nitrate eluant is about 1 *M* salt and 0. 1 *M* acid. At higher levels strongly sorbed anionic uranyl complexes of these anions are formed. A typical elution curve using a solution 0.9 *M* NaCl and 0.1 *M* HCl is shown in Fig. 4. The uranium is preceded from the bed by a sulfate band, which is shown by pH measurements to be sulfate, rather than bisulfate. The absence of uranium in this portion is an important point, as it allows a discard of sulfate to be made in order to prevent buildup of the sulfate in the recycled eluant system. The remainder of the solution can be precipitated directly with base to give a high grade concentrate. In some cases use is made of the "split elution" technique, in which the high-level portion of the eluate is precipitated and the low-level portion is recycled for use as the initial portion of eluant for the next column.

During the elution all of the sulfate on the resin is replaced by chloride, so that an equivalent quantity of chloride must be added to the eluant when it is recycled. Some, and perhaps all, of this requirement may be met with the acid which must be added each cycle to bring the acidity up to 0.1 *M*.

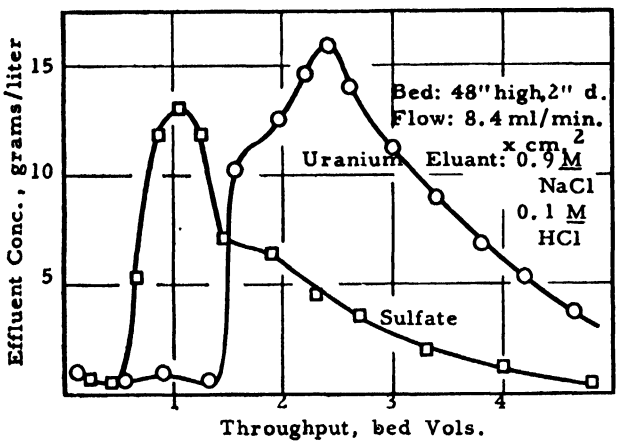

Figure 4. Elution of uranium and sulfate

Resin Poisoning

Although the interfering species referred to above are important, probably the most serious difficulty with this process has arisen from the presence in the leach solution of trace amounts of very strongly sorbed species. The effect of these species is not observed easily in the course of a few cycles, but the resin eventually becomes sufficiently loaded with these "poisons" so that its uranium capacity is seriously impaired. Three such poisons have been encountered and identified to date. In South African operations considerable difficulty is experienced as a result of the presence of both cobalticyanide and polythionates. On the Colorado Plateau molybdenum is a major problem in some ores. Once identified, poisons may sometimes be dealt with by one of a number of methods. Molybdenum can be eluted from these resins with moderately strong NaOH. Polythionates can be destroyed by oxidation in the original leach or can be eluted with NaOH and Na_2S solutions. Removal of cobalticyanide requires extensive treatment with either thiocyanate solutions or carbonate solutions followed by acids.

CARBONATE ION EXCHANGE PROCESS

In the carbonate system the ground ore is leached with about 5 to 10% sodium carbonate, usually at an elevated temperature. In most cases the ore is roasted before leaching, and in some cases an oxidizing agent is added. If vanadium is present in the ore, some will be leached with the uranium. The following analysis is typical of the leach solutions obtained.

Constituent	*Grams/liter*	
U_3O_8	1.79	as U(VI)
V_2O_5	2.70	as V(V)
$CO_3^=$	36.5	
HCO_3^-	12.0	
$SO_4^=$	12.0	
Cl^-	0.18	
Fe	0.015	
Al	0.0	
PO_4^{---}	0.6	

In order to recover both the uranium and the vanadium from these solutions by the conventional precipitation process, the carbonate must be neutralized with acid. The ion exchange process offers a method whereby the carbonate leach solutions can be re-used for a number of cycles.

Sorption of Uranium

The anion exchange process for the recovery of uranium from carbonate leach solutions is very similar to that for sulfuric acid liquors. Thus, when the solution is passed through the resin bed, a reaction of the following type takes place:

$$4RCl + [UO_2(CO_3)_3]^{4-} \rightarrow R_4[UO_2(CO_3)_3] + 4Cl^- \qquad (2)$$

Several resins were tested, but the quaternary amine resins were again found to give the best performance. A typical curve is shown in Fig. 5 for sorption of uranium on a column of Dowex 1 from a carbonate solution which did not contain vanadium.

The loading of the resin is affected rather critically by the pH of the solution. While resin loadings of 30 to 60 grams U_3O_8/liter resin were obtained from solutions at pH 10, only 10 to 15 grams/liter were sorbed from solutions at about pH 9. The presence of chloride also inhibited the sorption. Uranium could not be sorbed from leach solutions of ore that had been roasted with salt. An increase in temperature did not appear to affect the loading appreciably, but the slope of the breakthrough curve was steeper.

Most of the carbonate leach solutions produced on the Colorado Plateau contain considerable concentrations of vanadium. The sorption of uranium from such solutions by anion resins is greatly influenced by the vanadium since vanadium is held much more strongly by the resin. When the solution is passed through the resin bed, both values are sorbed. However, as the top of the column becomes saturated with vanadium, the sorbed uranium is replaced and a uranium front proceeds down the column ahead of the vanadium front. The solution between the uranium front and the vanadium front contains the uranium that has been eluted by the vanadium from the upper portions of the column in addition to the head concentration of uranium. Thus, after uranium breakthrough, the uranium con-

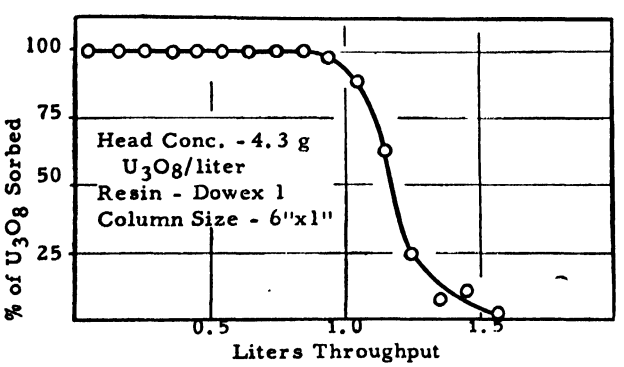

Figure 5. Sorption of uranium from carbonate solution

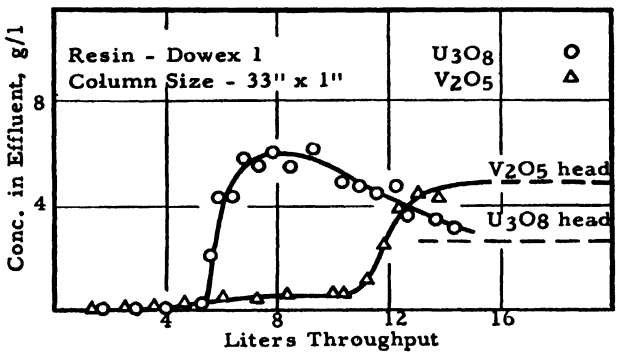

Figure 6. Sorption of uranium and vanadium from carbonate solution containing both values

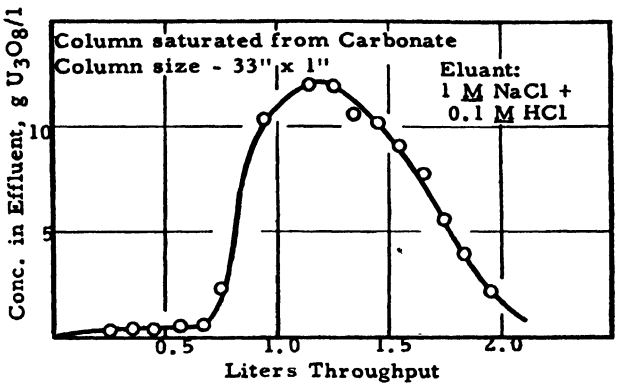

Figure 7. Elution of uranium from Dowex 1

centration in the effluent increases beyond the influent concentration.

Figure 6 shows a plot of the effluent concentrations of uranium and vanadium as functions of volume throughput for a typical leach liquor. There are three quite definite regions shown in this curve: a region in which both values are sorbed, a region in which vanadium is sorbed and uranium is eluted, and the region after vanadium breakthrough where both uranium and vanadium appear in the effluent. Two methods have been investigated for recovery of both values from the liquor. In one, the column is operated to uranium breakthrough and uranium and vanadium are then eluted selectively. In the other method, the column is operated to vanadium breakthrough, and the uranium-rich effluent is passed through a second column for uranium sorption.

Elution of Uranium

The most effective eluant solution for uranium in this system appears to be sodium or ammonium chloride solution about 1 *M* in chloride and about 0.1 *M* in HCl. Ammonium sulfate and ammonium carbonate solutions also removed uranium but not as completely as the acidified chloride solutions. A typical uranium elution curve is shown in Fig. 7.

When vanadium is present on the loaded resin, it is necessary to remove it before removing the uranium since otherwise both vanadium and uranium would appear in the eluate. Treatment with a saturated SO_2 solution reduced the vanadium to the tetravalent state and removed it completely from the resin.

Treatment of columns of ion exchange resin in the carbonate form with these acidic solutions results in considerable liberation of carbon dioxide in the resin bed. This gassing, however, can be minimized by pretreatment with a solution of dilute ($\sim 0.1N$) H_2SO_4 or with SO_2 gas before elution. Uranium can be recovered from the eluates by neutralization with ammonia. Several products have been obtained which after ignition assayed over 95% U_3O_8. Overall recoveries $> 95\%$ have been obtained.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the services of the analytical section under the supervision of Mr. Herbert O. Kerlinger and Mr. M. Dean Yeaman.

The Resin-in-Pulp Process for Recovery of Uranium

By R. F. Hollis and C. K. McArthur,* USA

There are under construction, or in the final design stage, in the United States, five commercial uranium ore processing plants incorporating the Resin-in-Pulp (RIP) process, which involves the recovery of dissolved uranium values from acid-leached pulps by strong base anion exchange resins. This paper describes the development of the process from the laboratory to the pilot plant.

Prior to the application of anion exchange to uranium ore processing, all recovery methods resulted in the precipitation of an impure uranium product which required additional upgrading before it could be refined. The ion exchange process, on the other hand, provides excellent selectivity for the extraction of soluble uranium from leach liquors so that high grade uranium concentrates can be produced directly. The discovery that uranium is readily adsorbed by anion exchange resins coupled with the experience of resin and equipment manufacturers in water treatment led to the rapid development and adoption of ion exchange in a multiple column type operation. At the present time many processing plants using fixed-bed ion exchange are in operation or under construction in Africa, Australia and Canada and to a limited extent in the United States.

Although the fixed bed process has been highly successful, the feed to the ion exchange columns must be a clear solution, which is obtained by means of filtration or by countercurrent decantation of leached pulps. With some ores, poor filtration or settling characteristics make the production of a clear solution difficult. Most processing plants in the United States receive their ores from a number of small mines and considerable variation occurs in the settling and filtering behavior of the ores. An ion exchange process was therefore desirable in which the uranium could be recovered directly from the leached pulp by adding ion exchange resin which could be then separated from the pulp by a screening operation. The process would thus resemble the cyanide-charcoal process in which gold is adsorbed from cyanide pulp by means of activated charcoal. Preliminary tests in which leached pulps were directly contacted with resin beads showed that such a process was entirely possible. Therefore a program was initiated which led to the development of the RIP process.

* National Lead Company, Inc., Raw Materials Development Pilot Plant, Grand Junction, Colorado.

PROCESS CHEMISTRY

The ion exchange process for uranium recovery from sulfuric acid leach liquors depends upon the high affinity of the uranium sulfate complexes for the anion exchange resin. It has been demonstrated that the uranium is adsorbed primarily as the trisulfate complex, $[UO_2(SO_4)_3]^{4-}$, and to a minor extent as the disulfate complex, $[UO_2(SO_4)_2]^{2-}$. In addition, there are found to be adsorbed appreciable amounts of sulfate and bisulfate ions.

All other things being equal, the adsorption of the disulfate complex is to be preferred, since it gives a higher uranium loading per unit amount of resin. In practice, however, it is not possible to adjust the feed composition in the required manner. The requirement for a high loading of disulfate complex is a high uranium to sulfate concentration ratio. The ores commonly encountered in the United States give leach solutions which are too low in uranium to meet the requirement.

It has also been found that uranium loadings increase with increasing pH. This follows from the fact that bisulfate has a greater affinity for strong base anion exchange resins than sulfate so that fewer resin sites are available for uranium adsorption in acid solutions where equilibrium favors the bisulfate.

The composition of leach liquors obtained from domestic ores varies considerably in uranium and sulfuric acid concentration. Typical leach solutions are adjusted to pH 1.0 to 1.5 and contain 0.5 to 1 gram U_3O_8 per liter and approximately 10 to 20 grams sulfate per liter prior to ion exchange treatment.

The recovery of uranium by ion exchange involves three basic operations:

Adsorption

The resin is contacted with the uranium-bearing solution, and the uranium is adsorbed. This operation is commonly referred to as the adsorption, loading or exhaustion cycle. The reaction whereby the uranium is adsorbed by the resin may be written in the following manner where R indicates the resin

$$4RCl + [UO_2(SO_4)_3]^{4-} \rightleftharpoons R_4UO_2(SO_4)_3 + 4Cl^-$$

$$2RCl + [UO_2(SO_4)_2]^{2-} \rightleftharpoons R_2UO_2(SO_4)_2 + 2Cl^-$$

Elution

The adsorbed uranium is removed from the loaded or exhausted resin by contacting the resin with an acidified chloride or nitrate solution. This operation is referred to as the elution cycle, the solution used for elution is called the eluant, and the resulting uranium-rich solution, the eluate. The elution reaction proceeds from right to left in the equations above.

Precipitation

The uranium is precipitated from the eluate by neutralization, and the barren filtrate is recycled for elution after adjustment of pH and chloride or nitrate concentration.

PROCESS VARIABLES

Adsorption by ion exchange is controlled by equilibria involving the concentration of the adsorbed species on the resin and the concentration of the adsorbable species in the solution. In a columnar bed system, the uranium concentration in the resin and in the solution decreases from top to bottom. Conditions are ideal for the necessary equilibria whereby simultaneous saturation of the resin and complete removal of the uranium from the solution are attained. However, in a batch type of contact, adsorption occurs only to the point where there is an equilibrium between the uranium on the resin and in the solution, and no concentration gradient exists in the resin or solution. Thus to insure complete recovery of uranium a number of individual stages or contacts is required, in each of which a fixed amount of uranium is adsorbed. Therefore, a fundamental difference between a column and a batch contact system is the number of stages available for adsorption. In a column, as in any packed tower, this number of stages is very large whereas in a system of individual contacts, the number must of economic necessity be small.

Other points of difference are in the choice of operating variables. The variables in a columnar system are the solution retention time and the total throughput of solution per unit volume of resin. These same variables exist in a batch contact system, but in addition the ratio of solution to resin may be any desired value. In a fixed bed columnar system, the ratio of solution to resin is determined by the void volume in the resin bed, which is approximately 40 per cent of the bed volume.

To evaluate the applicability of batch contact operation to uranium processing, laboratory experiments were performed on clear solutions. These experiments showed that the resin can attain the same degree of saturation by repeated batch contacts as is possible in columns. Likewise, by repeated contacts with fresh resin, a uranium-bearing solution can be as completely stripped of its uranium content as in columnar operation. Finally, by repeated contacts with a one molar nitrate or chloride solution, a resin loaded with uranium can be completely stripped of its uranium content.

Additional batch contact experiments showed that uranium is readily adsorbed directly from leached pulps by anion exchange resins and that the U adsorption rate is essentially unaffected by ore solids.

However, no data were available on the effect of contact time, solution to resin ratio, and number of stages on uranium adsorption. An investigation of these variables was required before further development of the RIP process was possible.

The effect of contact time and extent of loading was studied in a series of tests in which 10 ml of resin were contacted for two hours with ten successive 250 ml portions of leach solution. The data are presented graphically in Fig. 1. From these data, two main conclusions can be drawn. First, the time required to reach steady state is short; well over 50 per cent of the uranium that can be adsorbed is picked up by the resin within the first 10 minutes of contact and steady state is reached in about 40 minutes. Second, the uranium loading on the resin has no apparent effect on the time required to reach steady state.

Tests were run to see how much difference there was in resin loading in a multiple contact batch adsorption system when 5- and 15-minute contacts were used instead of the 40-minute contacts previously found necessary to attain steady state loading. Three portions of 10 ml of resin were contacted with ten 250 ml portions of an artificial uranium solution for 5, 15 or 40 minutes. Figure 2 presents the cumulative uranium loading on the resin versus the total contact time. The data show that 95 and 81 per cent of the steady state loading was obtained respectively with the 15-minute contacts and the 5-minute contacts. A suitable retention time would thus be 15 minutes; longer retentions are unnecessary.

In Fig. 3 the results of tests are presented in which several one liter portions of leach solution were contacted for two hours with different amounts of resin. The data show that the time required to reach steady state was essentially unaffected by the ratio of solution to resin.

In the preceding experiments, the resin was contacted batchwise. In a commercial operation, the flow of solution would be continuous whereas the

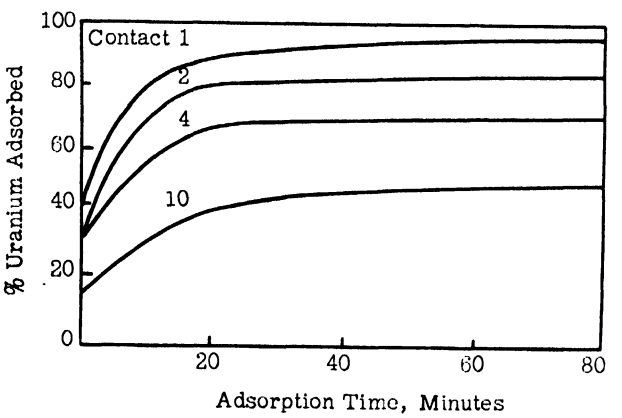

Figure 1. Effect of successive contacts on uranium adsorption

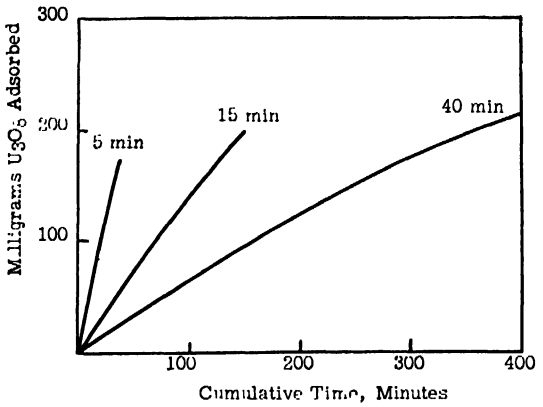

Figure 2. Effect of cumulative contacting on uranium adsorption

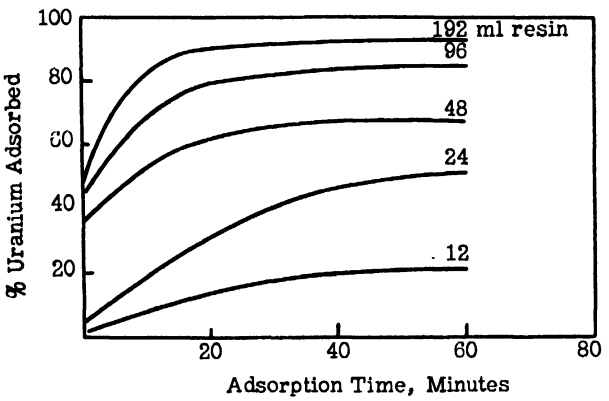

Figure 3. Effect of solution to resin ratio on uranium adsorption

resin would be intermittently advanced countercurrently. By analogy to column operation, the resin in the first stage should reach saturation when the effluent from the last stage reaches a uranium concentration of approximately 2 per cent of the feed concentration (cutoff). The data in Table I summarize the results of experiments simulating commercial operation in which the effect of solution to resin ratio and solution retention time were studied.

Table I. Effect of Solution Retention Time and Solution to Resin Ratio on Rate of Uranium Adsorption and Number of Stages Required

Solution retention time in minutes	*Solution to resin ratio*	*Stages required*	*U_3O_8 adsorption rate, mg U_3O_8 per ml resin/minute*
4	2.4	6	0.104
4	5.1	7	0.328
4	10 2	9	0.548
4	4.0	7	0.273
7.5	4.0	6	0.170
15.0	4.0	5	0.102

The data show that the number of stages required for saturation of the resin to occur simultaneously with cutoff increases as the solution to resin ratio increases and as the solution retention time decreases. At the same time, the quantity of uranium adsorbed per minute per ml of resin increases with increasing solutions to resin ratios and decreasing solution retention time. Obviously, then, maximum resin utilization would be obtained by the use of a large number of stages with high solution flow rates and solution to resin ratios.

There are two factors which will establish economic limits for solution to resin ratio and solution retention time. The first factor is the number of stages. As the number of stages increases, the size of the cell will decrease; but the capital cost will increase because it is generally cheaper to build a large cell rather than several small cells of the same total capacity or solution retention time. The second factor is timing. After the resin has been loaded, it must be removed from the adsorption circuit and eluted. This requires time. Consequently, if loaded resin is being removed from the adsorption circuit faster than it can be eluted, additional equipment and resin inventory is required.

The elution of uranium from loaded resin proceeds because of the high concentration of adsorbable anion in the eluant and is subject to the same considerations which affect uranium adsorption. In uranium elution two requirements must be met. First, the uranium must be completely removed from the resin, otherwise the residual uranium will be lost during the succeeding adsorption cycle. Second, the uranium should be contained in the smallest practical volume of solution so as to reduce subsequent precipitation costs.

Table II summarizes the results of batch contact tests to determine the effect of solution to resin ratio and contact time on the number of contacts required to obtain complete elution. Complete elution of uranium is usually considered to have occurred when the concentration of the uranium in the last fraction of the eluate does not exceed 0.1 gram per liter. The eluant used in these tests was 0.9*M* NH_4NO_3–0.1*M* HNO_3. From Table II it is evident that higher grade eluates are obtained if the solution to resin ratio is reduced. However, as the ratio becomes smaller, the number of stages required for complete elution increases.

The above data were obtained from successive batch contacts with fresh eluant. The data in Table III present the results obtained in a batch countercurrent system where fresh eluant was introduced only in the last stage of the elution circuit. The

Table II. Effect of Solution to Resin Ratio and Number of Contacts on the Eluate Grade

		Eluate gm U_3O_8/l			
		32-minute contact			*16-minute contact*
Contacts	*Ratios*	*1.4*	*2.8*	*5.6*	*5.6*
1		6.58	5.75	3.32	2.74
2		5.95	2.70	0.93	1.29
3		2.51	1.45	0.24	0.50
4		1.85	0.27	0.08	0.21
5		0.65	0.11	0.02	0.04
6		0 50	0.05		0.01
7		0.20			
8		0 16			

solution to resin ratio in these tests was 5.6 and the contact time was 32 minutes per stage.

Table III. Four Stage Batch Countercurrent Elution Test

	Eluate U_3O_8 gm/l	
Cycle	Stage 1	Stage 4
0	6.7	0.01
1	7.0	0.01
2	6.9	0.01
3	6.9	0.003

Comparison of Tables II and III indicates that countercurrent movement of the eluant does not appreciably affect elution efficiency, but does materially improve eluate grade. The actual data presented indicates a twofold increase in the U_3O_8 concentration of the eluate. Thus the cost of alkali for precipitation of uranium from eluate would be almost halved. Further increases in the uranium concentration of the eluate may be obtained by increasing the number of stages.

PROCESS DEVELOPMENT

In the initial experiments which led to the development of the final RIP process, standard anion exchange resin beads were added to a leached pulp and later removed by screening or, alternately, the resin was placed in a stainless steel wire mesh basket which was gently agitated in the pulp. The fine size of the beads, predominately 20/48 mesh (0.30 – 0.83 mm), necessitated the use of screens having an opening no larger than 65 mesh (0.20 mm), and the transfer of the pulp through the screen was difficult. A program of resin development was therefore undertaken in cooperation with commercial resin manufacturers to produce ion exchange resins in a form which could be readily separated from the pulp by a coarse screening operation. The resin forms developed were of two shapes: thin sheets and extruded $\frac{1}{16}$-in diameter rods. A magnetic resin was also prepared by incorporating finely ground magnetite into the sheet or extruded forms. The adsorption characteristics and physical stability of these new resin forms proved to be generally unsatisfactory. Efforts of the resin manufacturers were then directed to the production of coarser bead resins having a predominately $\frac{10}{20}$ mesh (0.83 – 1.65 mm) thus permitting a separation of resin from the pulp with a screen having a nominal 28 mesh (0.59 mm opening). Early lots of these coarser bead resins had generally low chemical efficiency and physical stability. During the past two years, large bead resins have been improved so that today their chemical and physical stability is comparable with that of the standard bead resins.

With the successful production of coarse bead resins, the RIP process was an actuality. However one more link in the chain was necessary—the development of a mechanical method for conducting the basic adsorption and elution steps. This mechanical method would have the following requisites: (1) close metallurgical control; (2) minimum resin loss (mechanical and attrition); (3) constant control of resin to pulp and resin to eluant ratios throughout the system; (4) applicability to type of resin beads available; (5) low maintenance and operating costs; (6) simplicity and flexibility of operation; (7) low capital cost; (8) capability of expansion from small units to larger plant scale models without sacrifice in efficiency.

It was recognized quite early that all of the preceding requirements for good resin-in-pulp operation probably could not be incorporated in the first machine developed for an operating plant. It was apparent, however, that close metallurgical control, minimum resin loss, and control of resin to pulp ratios were absolutely essential and could not be sacrificed. These three basic requirements had more bearing on the selection or rejection of proposed machines than any other factors. It was further established that a machine designed to operate in a desanded pulp had the best chance of success because of superior screening efficiency. As a result, the work was concentrated on desanded pulps in order to speed up development of the process.

Two basic schemes were given consideration in initial equipment development studies. The first scheme was one in which the resin actually moves continuously and countercurrent to the flow of pulp in the adsorption cycle and continuously and countercurrent to the flow of eluant in the elution cycle. The second scheme involved a modified countercurrent system in which the resin is confined to containers or units through which the pulp or eluant flows, the countercurrent effect being produced by intermittently advancing each unit in its respective circuit.

A thorough screening process of many suggested devices narrowed the choice to two machines each typical of the two schemes noted above. The procedure having the characteristics of a continuous countercurrent system was a system of trommels and agitators in which the resin beads were advanced from tank to tank by elevating with lifter bars. This method had the advantage of continuous operation and low capital cost. Work was suspended on it, however, in favor of a basket machine arrangement as it was not certain that the trommel arrangement would provide the most important requisites for successful operation, namely, metallurgical control, low resin loss and positive control of resin to pulp ratio.

The basket arrangement, which ultimately was installed in the pilot plant at Grand Junction, Colorado, in early 1953, was an adaptation of the modified intermittent countercurrent scheme. The development of the basket machine strangely enough began in the laboratory where bench scale batch loading and elution tests were made to prove the applicability of RIP. Cloth bags and small wire baskets containing the beads were slowly moved up and down in containers of pulp or solution and advanced intermittently. The basic principle employed in the pilot

plant is no different than that used in the early and seemingly primitive methods which demonstrated the process was possible. Baskets in the present machines are slowly moved up and down for the same basic reasons, namely, to contract and expand the bed of beads so that satisfactory contact with the pulp can be effected. At the same time mild agitation is produced which improves circulation and prevents settling of solids within and without the basket.

Figure 4 is a sketch showing the construction details of a basket, units of which range in size from 17 in. × 17 in. × 17 in. to 72 in. × 72 in. × 72 in. The 17-in. baskets operate with fourteen 6-in. strokes per minute; the larger 72-in. machine, with a 20-in. stroke. Wet settled resin depth varies in the machines from approximately 6 in. in the 17-in. machine to 16 in. in the 72-in. unit.

Figure 5 shows a cross section of a basket in its tank and illustrates the position of the beads at the bottom and top of the stroke. Note the slot on each side of the basket. A pumping action takes place due to the motion of the basket which elevates the pulp through the slot from the bottom of the cell to the top.

The first unit installed in the pilot plant contained six stages or banks. Each bank contained four baskets separated into compartments by baffles. The

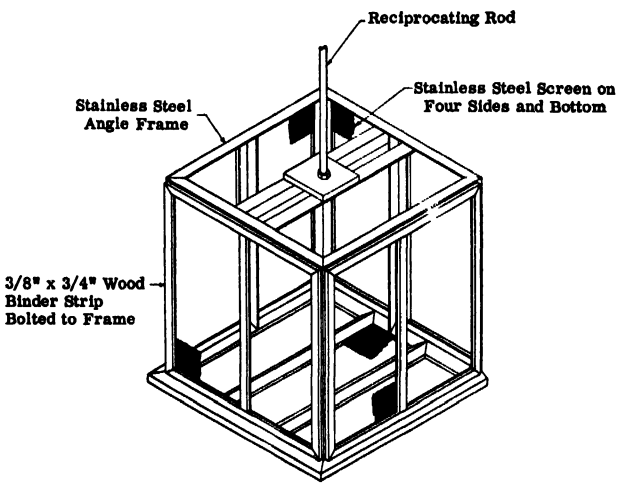
Reciprocating Rod
Stainless Steel Angle Frame
Stainless Steel Screen on Four Sides and Bottom
3/8" x 3/4" Wood Binder Strip Bolted to Frame

Figure 4. Isometric view—18-in. basket

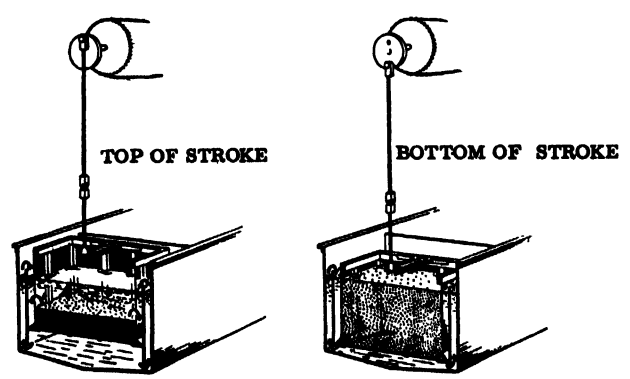

Figure 5. Section through basket, showing expansion and compaction of beads in adsorption units

baskets were constructed of a hard maple framework rigidly supported and held together by tongue and groove joints. The top of the basket was left open with the remaining five sides enclosed with Ludlow Saylor No. 281, 8 × 28 mesh Rec-Tang Screen bolted to the framework. The bolts were 18-8 stainless steel and the screen was woven with Carpenter 20 stainless steel wire.

The baskets were actuated in pairs by ¼-hp gear motors. These gear motors were connected to a shaft by a chain drive. On the ends of the shaft were eccentric plates upon which was bolted a crank pin. The rotation of the shaft was translated into a vertical movement of the basket by means of a connecting rod. No guides were provided on the first design and each basket was allowed to move up and down freely within the confines of its compartment. Length of stroke on this machine was made adjustable by the drilling of several holes in the eccentric plate at various distances from the center line of the shaft. The speed of the baskets could be varied by changing the sprocket ratios on the chain drive.

Early test work both in the pilot plant and in the laboratory indicated that the original six bank system did not provide sufficient flexibility. It was necessary to load with five banks on the exhaustion cycle while the sixth bank was being eluted in a six-contact batch countercurrent process. A great deal of fundamental information and operating experience was obtained from this original basket installation however, and the results were so encouraging that a new and larger plant was built in 1954.

From the experience and metallurgical data accumulated in the original installation certain improvements were made with respect to details in design and bank arrangement.

Figures 6 and 7 are schematic and pictorial pilot plant flowsheets from the grinding unit through the RIP section.

This is a typical layout and represents almost exactly the flowsheets planned for the five processing plants which will incorporate the RIP process. The ore is ground in a ball mill and the pulp overflows the classifier at 50 per cent solids. This pulp is pumped to acid-proof Deveraux agitators and leached with sulfuric acid. The desanding operation then follows with four drag classifiers using two cyclones in parallel with the first two classifiers. This produces a –325 mesh slime containing approximately 8 per cent solids which is pumped to the RIP units. Since the concentration of dissolved uranium in the pulp being fed to the RIP circuit affects the operation of the adsorption section, efforts should be made to avoid unnecessary dilution of the feed. Thus the amount of water added should not be in excess of minimum requirements for washing the sands and adjusting the pulp density. The dilution water added during classification normally acts to increase the pH of the feed to approximately 1.5. The flow rate of the RIP feed depends upon the slime content of the ore, but the average is found to be about 0.65

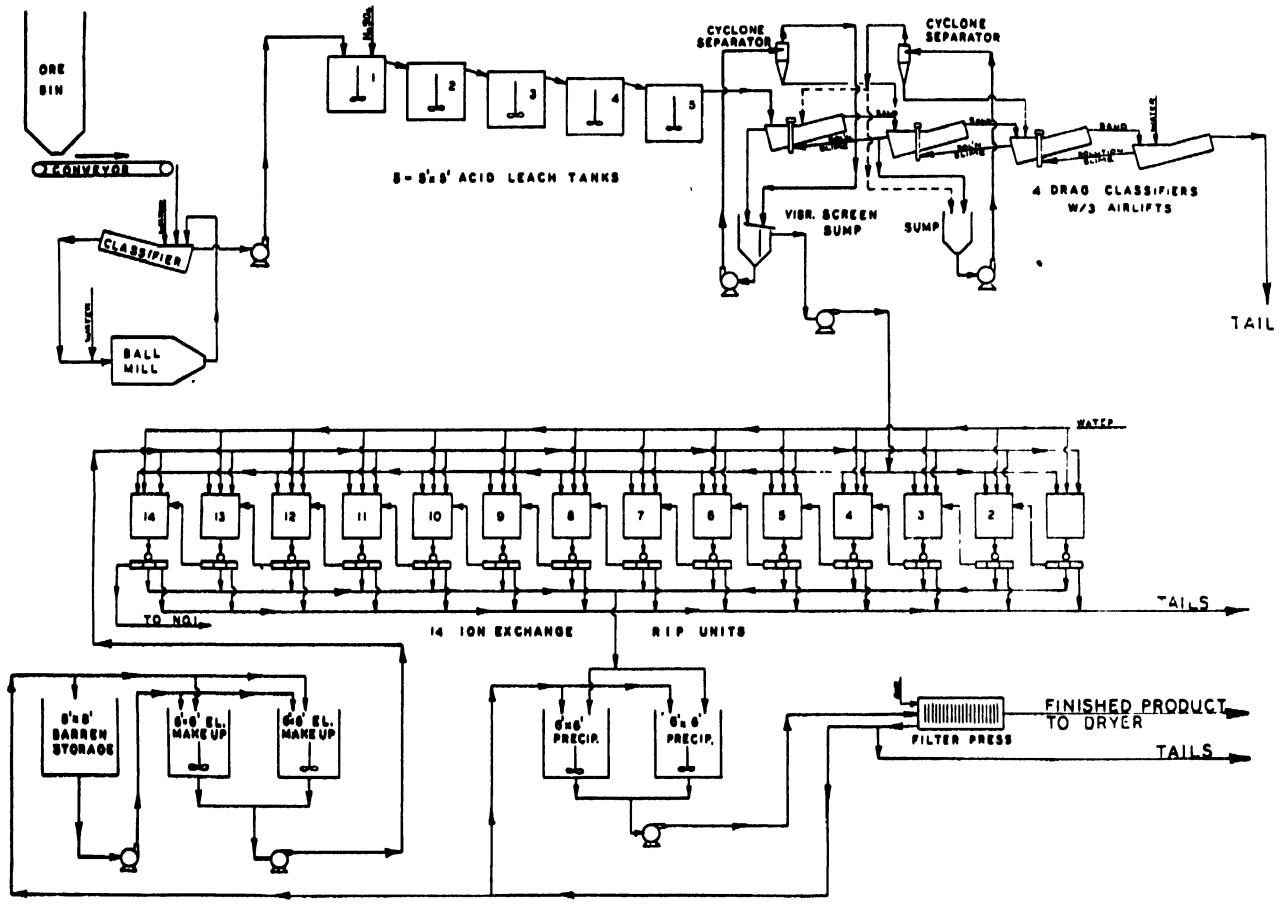

Figure 6

gallons per minute per ton of ore that is treated per day.

Information gained in the original pilot plant installation and data obtained in the laboratory had demonstrated that the following conditions are conducive to good operation and metallurgy in basket RIP:

1. The volume ratio of pulp to wet settled resin should be approximately 6 to 1.
2. The minimum number of banks on exhaustion for a normal pulp should be six; a maximum of nine could be used for low grade pulps and high flow rates.
3. The total pulp residence time, with six banks on exhaustion, should be approximately 100 minutes.
4. The minimum number of banks on elution should be six.
5. The feed pulp to the exhaustion circuit should contain less than 10 per cent solids and should be essentially all –325 mesh (less than 43 microns).

On the basis of the above requirements, the new RIP circuit was designed with 14 two-cell banks. Thus, under normal conditions, the circuit can be operated with six banks on exhaustion and six on elution with two banks as spares to permit changeover. A detailed drawing of an individual two-cell bank is shown in Fig. 8.

OPERATION OF THE PILOT PLANT RIP CIRCUIT

The principal operating variable for an RIP circuit is the length of time between changeovers. This time is determined by the rate of introduction of uranium to the circuit and the uranium capacity of the ion exchange resin. In the pilot plant RIP units, each of the fourteen banks contains two cubic feet of resin which has a capacity of about three pounds of U_3O_8 per cubic foot. When all banks in the adsorption section have been operated for some time and are at steady state, the lead bank will become saturated every three hours. When this occurs, the feed stream is switched from the lead bank to the second bank, and the pulp remaining in the lead bank is discharged and rinsed through the rest of the banks in the series. At the same time, a new bank, containing barren resin, is added to the tail end of the adsorption section, the overflow going to tails.

At the time of the changeover, the last bank should still be making a satisfactory barren and its performance determines the number of banks to keep on exhaustion. If tails are high at the time of changeover, obviously it is necessary to put an additional bank on exhaustion, or reduce the uranium throughput per cycle.

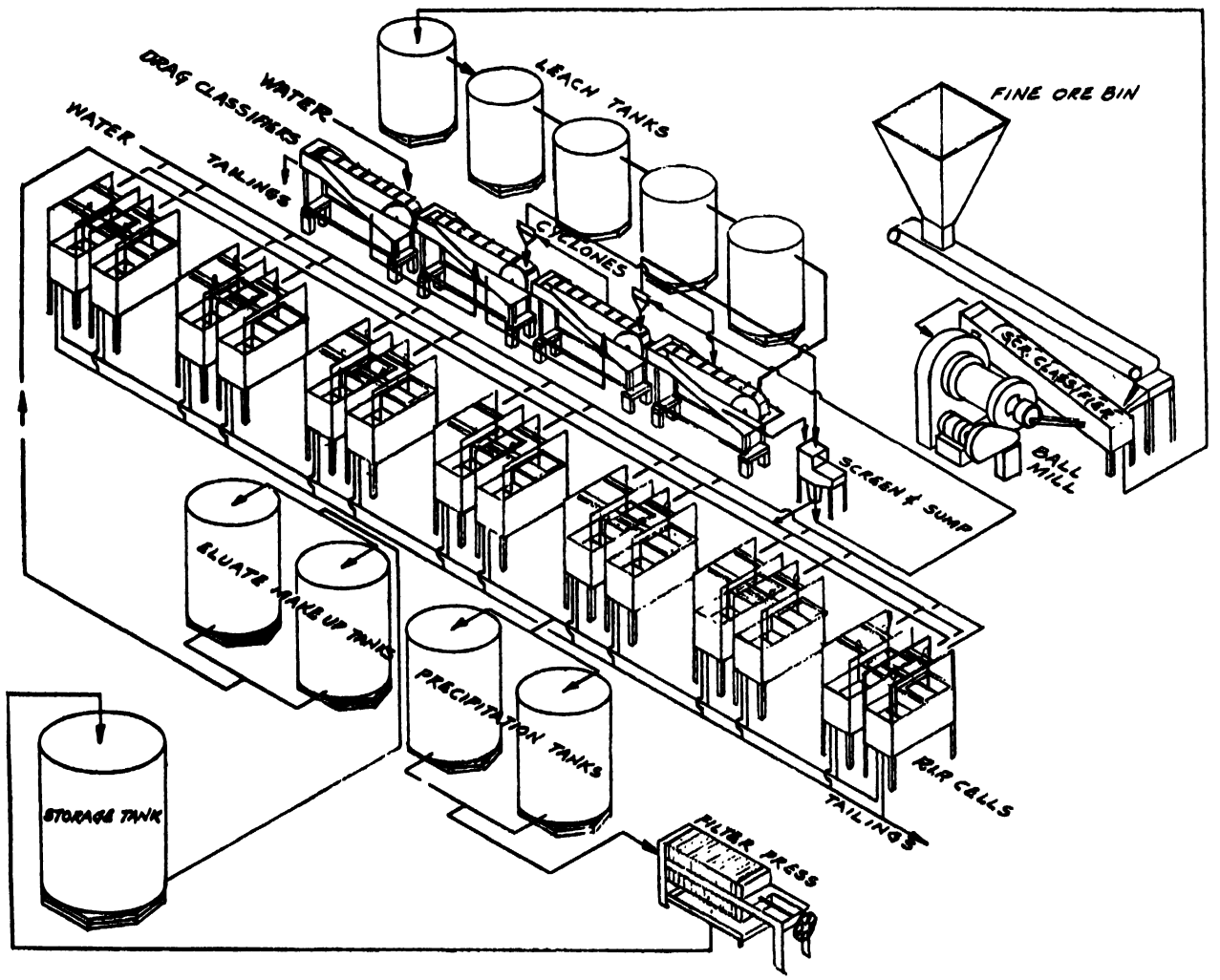

Figure 7. Resin-in-pulp flow sheet for treatment of uranium ores

The elution operation is controlled by the volume of eluant necessary to completely elute the uranium from one bank of loaded resin. As the elution cycle starts, the six banks in the elution section are full of eluting solution. A seventh bank, which contains loaded resin just taken off adsorption, but no solution, is added to the downstream end of the elution section. The solution in each bank is now transferred one bank downstream. The flow so produced fills the newly added bank and empties the lead bank. The resin in the empty bank is rinsed free of entrained eluant and the rinse water is pumped through the circuit. The empty bank is now removed from the elution section and placed on standby for use in the adsorption section. Barren eluant is next pumped into the new lead bank, displacing solution from bank to bank until an equivalent volume of uranium rich eluate is discharged from the last bank into the precipitation tank. The volume of barren eluant pumped into the system is determined by the uranium concentration in the discharge from the lead bank. When its concentration drops to 0.1 gram U_3O_8 per liter, the flow of eluant through the system is stopped until the next changeover. In the pilot plant RIP circuit, approximately 86 gallons of eluant are used per changeover. Pulp and eluate transfers are made by a system of airlifts. A cutaway drawing of the airlift arrangement is shown in Fig. 9. The airlift discharges into a distributor which provides for transfer to the tailings pond, to the next bank downstream, or to the precipitation tank.

The pregnant eluate which normally contains eight grams of U_3O_8 per liter is precipitated by neutralizing with ammonia or magnesia. The resultant slurry is filtered and washed in a filter press. The washed cake is then dried in a tray drier. The barren filtrate is adjusted to 56 grams nitrate per liter by addition of ammonium nitrate and then acidified to pH 1.2 with sulfuric acid. Total reagent consumption per pound of U_3O_8 recovered will vary with the degree of saturation of the resin. Pilot plant operating data indicate an average consumption of 3.8 pounds ammonium nitrate, 1.8 pounds sulfuric acid, and 1.0 pound of ammonia.

Typical RIP operating conditions with respect to uranium distribution are shown in Fig. 10, 11 and 12. These figures are based on conditions prevailing at the time of changeover. Figure 10 illustrates the gradual drop in resin loading from the lead bank to

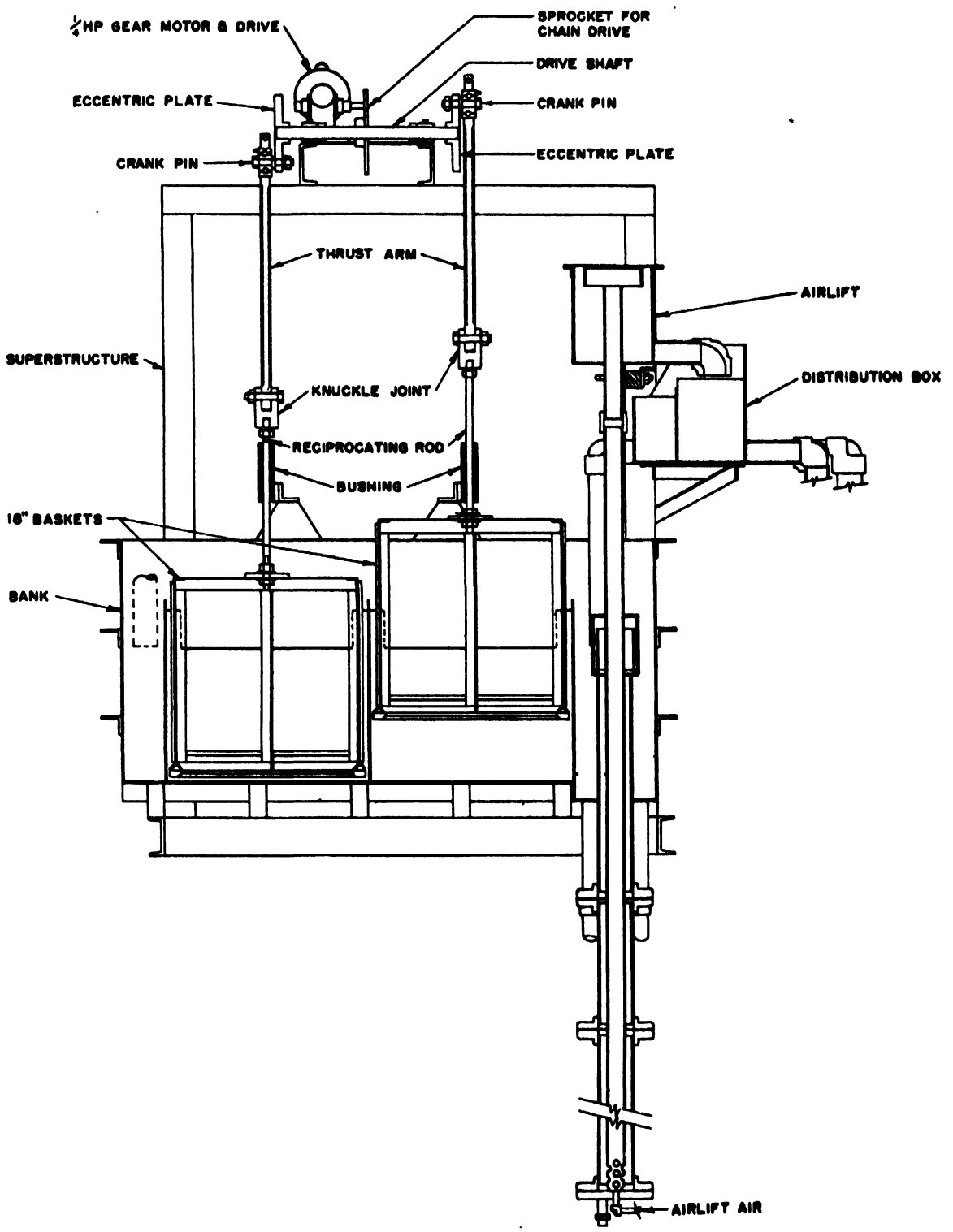

Figure 8. Section view of two-cell bank

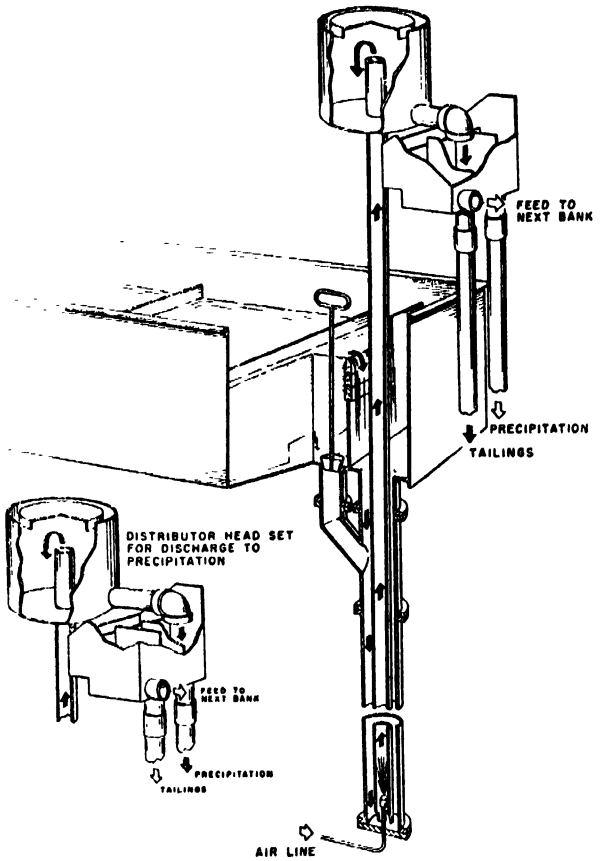

Figure 9

the tailings bank in a seven bank adsorption section. Figure 11 shows how the solution grade in the same section decreases as the feed passes from bank to bank and how the uranium distribution coefficient increases with decreasing solution grade.

Figure 12 illustrates how the resin loading varies from bank to bank through out a seven-bank elution section.

During two years of RIP pilot plant operation, equipment performance has been remarkably trouble-free. At no time has it been necessary to shut down for mechanical failure of the RIP units. The original baskets, which are of wooden construction, are still in operation, and no screen changes have been necessary. Mechanical stability of the large bead resins has been found to be exceptionally good. The total resin loss due to attrition in two years of operation has been 23 per cent. During this two-year period, the resin was actually on stream for 8070 hours. Loading capacities have decreased approximately 10 per cent, but adsorption and elution rates appear to be unaffected.

No serious process difficulties have been encountered since the first pilot plant demonstration of the RIP process. However, if the ore being processed contains vanadium it is necessary to be sure that the dissolved vanadium is present in the reduced form. Pentavalent vanadium adsorbs on the resin and is not eluted by the regular elution solution. The adsorption of vanadium is not permanent as it can

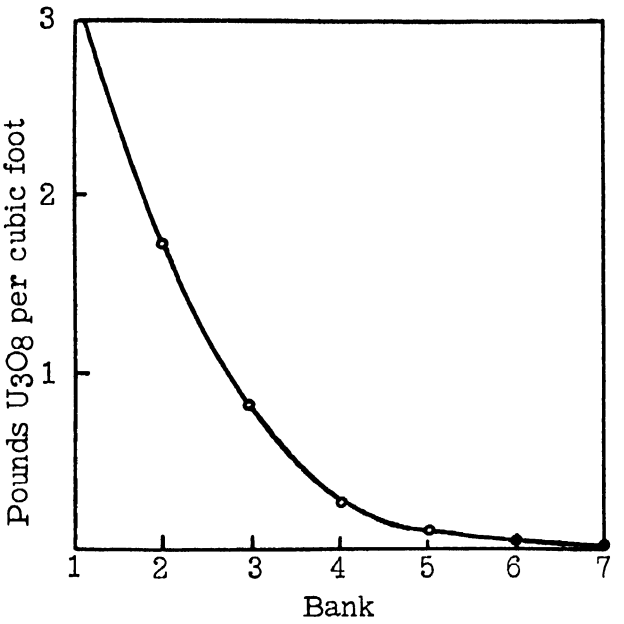

Figure 10

be stripped from the resin by the use of sulfurous acid. However, the best solution to the problem is to avoid its being adsorbed. To insure that the vanadium is in the (IV) oxidation state in the pulp, sufficient powdered iron is added at the end of the leach to produce a terminal emf of 0.45 volts (vs Standard Calomel electrode).

COMMERCIAL DESIGN CONSIDERATIONS

An example of the factors which must be considered in the design of a commercial size mill will now be presented. Assume, that it is necessary to design an RIP circuit for a mill treating 450 tons per day of ore containing 0.3% U_3O_8. To determine the number and size of baskets needed in the RIP circuit the following procedure would be employed:

1. Estimate the cycle time. Pilot plant test work has indicated that a minimum cycle of two hours can be used. For design a 3-hr cycle is assumed.

2. Determine the uranium imput per cycle. Since 450 tons of ore are to be processed per 24 hours, 56.2 tons of ore are being fed to the leach circuit

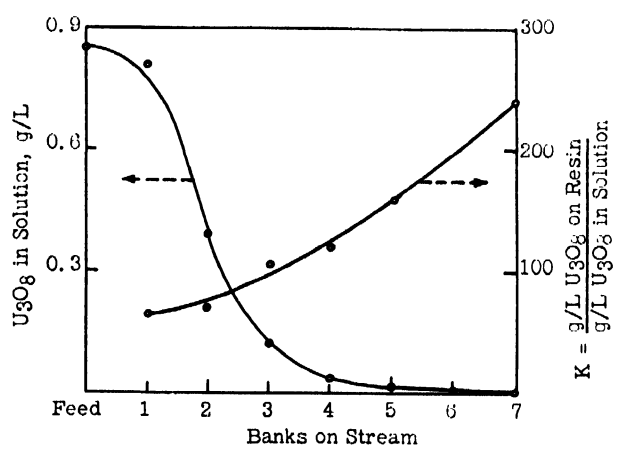

Figure 11

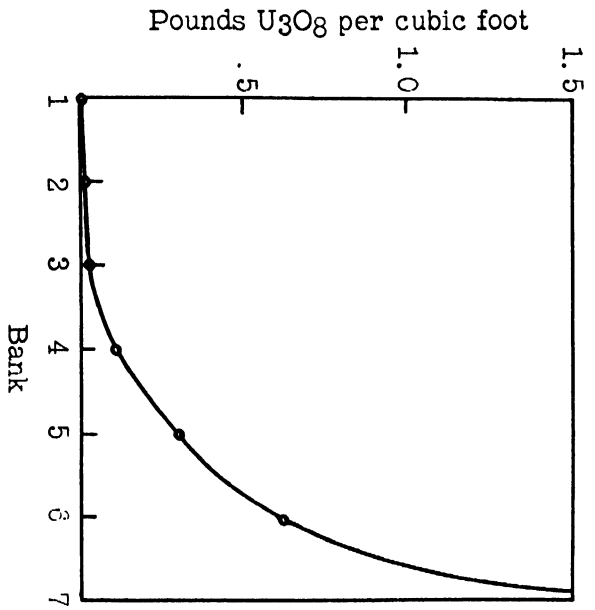

Figure 12

every three-hour cycle. This is equivalent to 337 pounds of U_3O_8 for an ore containing 0.3 per cent U_3O_8. Assuming, in this instance, a 90 per cent solubilization, then 303 pounds of U_3O_8 will be introduced into the RIP circuit every cycle.

3. Determine the resin inventory per bank. For a resin with an operating capacity of 3 pounds of U_3O_8 per cubic foot, 101 cubic feet will be required per bank, since during each cycle one bank containing 303 pounds of U_3O_8 must be removed from the adsorption section.

4. Determine the number and size of baskets per bank. To date the maximum size basket which has been constructed and tested has been a unit 6 ft × 6 ft × 6 ft. A basket of this size has operated efficiently with a resin inventory of 50 cubic feet. Thus each bank would consist of two 6-ft baskets.

5. Determine the total number of banks in the circuit. As indicated earlier, a minimum of fourteen banks is required for efficient operation and flexibility. This assumes six or seven banks on exhaustion and six on elution and one or two on standby. With very low grade feed, however, the requirement may increase to sixteen banks in order to provide for high recovery and efficient elution.

Wherever possible, the number of banks required should be determined from pilot plant tests.

DISCUSSION

Results obtained in the pilot plant testing of the RIP process on the ores from seven different ore producing districts of the United States has resulted in the RIP process being incorporated in all of the new plants now under construction or in the design stage. RIP represents the successful solution to a problem that has been studied as long as hydrometallurgy has been practiced, namely the elimination of the liquid-solid separation before recovery of the dissolved values. The advantages of the RIP process are: (1) complete independence from the physical properties of the ores such as filtering and settling characteristics; (2) better than 99 per cent recovery of the dissolved uranium values; (3) a final product that averages 70 per cent U_3O_8 or better and is largely free from elements which would be deleterious to processes used in the refining of uranium metal; (4) low mechanical maintenance costs; (5) dependable mechanical and metallurgical operation resulting in a high percentage of operating time; (6) flexibility with regard to tonnage of ore treated as the capacity within limits is based on uranium throughput.

FUTURE DEVELOPMENTS

At the present time the RIP process is being applied to the recovery of uranium from alkaline leached pulps. Test work is currently in the pilot plant stage; although several process problems exist, highly encouraging results have been obtained.

Equipment for a continuous countercurrent RIP process, in which the resin is moved continuously rather than batchwise, is in the pilot plant stage of development. In addition the recovery of uranium from desanded pulps in fixed bed columns is being investigated.

ACKNOWLEDGEMENTS

The authors are pleased to acknowledge the contributions of the following persons in the development of the RIP process:

Dr. G. G. Marvin, Assistant Director, Division of Raw Materials, US Atomic Energy Commission, who has actively supported and encouraged the activities of the Raw Materials Development Laboratory and its pilot plant.

Dr. A. M. Gaudin, Richards Professor of Mineral Engineering, Massachusetts Institute of Technology, under whose direction the original process development was carried out.

Mr. D. M. Kentro, Metallurgical Advisor, Division of Raw Materials, US Atomic Energy Commission, and formerly Director, Raw Materials Development Laboratory, who encouraged the development of the process in the original pilot plant.

Mr. J. S. Breitenstein, Technical Director, Raw Materials Development Laboratory, under whose direction the new RIP installation was constructed, and who has given continuing encouragement to the furtherance of the process on a commercial scale.

The technical staff, past and present, of the Raw Materials Development Laboratory, whose test work provided the fundamental information which culminated in the development of the process.

Mr. D. R. George, Dr. A. M. Ross, and Dr. M. A. DeSesa who provided technical assistance in the preparation of this paper.

An Ion Exchange Process for the Recovery of Uranium from Carbonate Leach Solutions

By Jagdish Shankar, D. V. Bhatnagar and T. K. S. Murthy,* India

Recovery of uranium from low grade ores is generally achieved by a leaching process which takes advantage of the fact that most of the uranium minerals are soluble in both acid and alkaline solutions. The alkaline leaching process employs sodium carbonate solution which extracts the uranium as the uranyl carbonate complex $Na_4[UO_2(CO_3)_3]$. The commercial success of this process depends on an efficient method of recovering uranium completely and economically from the leach solutions and recycling the barren liquors. The conventional method of recovering uranium by precipitation with sodium hydroxide was studied in detail by Forward and Halpern[1] and Bhatnagar and Murthy.[2] It was found that the method worked well when the uranium concentration in the leach solution was of the order of 2.5 gm/l. In the case of more dilute solutions (e.g., leach solutions obtained from low grade ores, assaying about 0.1% U_3O_8) the recovery of uranium was low and the reagent consumption high. In view of the relative simplicity of operation the caustic precipitation method has been widely used. In order to recover uranium from very dilute leach solutions preconcentration is necessary to bring the uranium content up to more than 2.5 gm/l.

Ion exchange resins are successfully employed for the concentration and recovery of metals from dilute solutions.[3,4] Uranium is present in the carbonate solutions as the quadrivalent complex anion $[UO_2(CO_3)_3]^{==}$ The present investigation was undertaken to see if an anionic exchange method could be developed for concentrating uranium from dilute solutions. In what follows are given the results of a study of the adsorption of uranium on a strongly basic resin—Amberlite IRA-400, and also that of other anions such as vanadate, phosphate and aluminate which are most likely to occur in carbonate leach liquors. The preliminary data was collected using solutions made from pure chemicals and the results confirmed with leach solutions obtained from a low grade uraniferous ore.

CAPACITY OF THE RESIN FOR COMPLEX URANYL CARBONATE

A batch of the commercial grade resin in the chloride form was sieved and the portion retained on British Standard Sieve 60 and passing BSS 20 was chosen. About 50 gm resin was thoroughly regenerated by passing 10% sodium chloride solution at 100 ml per hour in a column 23 mm diameter, washed with distilled water till only a trace of chloride could be detected in the effluent and back washed with distilled water to remove any fines still remaining. The resin was then removed from the column, air dried for 72 hours and stored in a stoppered bottle. The moisture content was determined by drying a sample in an oven at 110°C for 6 hours. The results of all experiments described below are based on the dry weight of the resin.

The conversion of the resin from the chloride to the nitrate form was used to measure its capacity for the $Cl^- \rightarrow NO_3^-$ exchange. The equivalent of one gram dry weight of the resin chloride was eluted in a small column with 10% sodium nitrate solution till the effluent showed no trace of chloride. The released chloride determined by titration against standard silver nitrate gave a capacity of 3.33 meq.

While the total capacity of the resin remained the same irrespective of the feed composition, the amount of uranium taken up would be expected to depend on the concentration of other ions in the feed. The capacity of the resin for the uranium complex when present in sodium carbonate solutions of different concentrations was, therefore, determined with the help of a series of break-through experiments. Sodium carbonate solution of known concentration containing uranium (added as uranyl nitrate) was passed through a column (0.9 cm diameter) containing 1.0 gm resin at a rate of 100 ml per hour. The passage of the solution was stopped when the concentration of the metal in the effluent was equal to that in the influent. The resin was then washed with 50 ml distilled water, transferred quantitatively into a platinum dish and destroyed by ashing. Uranium was then determined in the residue. The results obtained for the uranium uptake with varying concentrations of sodium carbonate are given in Table I.

The lowered uptake of uranium by the resin with increasing sodium carbonate concentration in the influent could be easily explained as the exchange

$$2R \cdot Cl + CO_3^{=} \rightarrow R_2CO_3 + 2Cl^-$$
(Resin chloride) (Resin carbonate)

would be favoured to a greater degree by increasing carbonate concentration. Since total capacity of resin is constant less uranium would be taken up.

* Atomic Energy Establishment, Trombay.

ADSORPTION BEHAVIOUR OF OTHER ANIONS

The commonly encountered impurities in carbonate leach solutions are the anions vanadate, phosphate, aluminate and silicate. The adsorption behaviour of some of these anions was investigated by passing synthetic solutions containing known amounts of these ions.

Table I. Capacity of the Resin for Uranium Complex—Effect of Sodium Carbonate Concentration. Uranium Concentration in the Influent, 50 mg U_3O_8/l

Concentration of Na_2CO_3 in the influent (gm/liter)	*Capacity (mg U_3O_8/gm dry resin)*
1.0	274
2.5	221
5.0	200
10.0	191
30.0	163
50 0	130
100.0	100

One gram column of the resin was prepared and through it was passed a solution containing 50 gm Na_2CO_3, 500 mg U_3O_8, 500 mg V_2O_5 and 500 mg P_2O_5 per liter at a rate of 100 ml per hour. 100 ml fractions of the effluent were collected. The results of analysis of each fraction, plotted in Fig. 1, show that the small amounts of vanadium and phosphorus taken up by the column during the passage of the first 100–200 ml of solution were subsequently displaced.

Aluminium dissolves to a lesser extent in cold 5% Na_2CO_3 solution than either vanadate or phosphate. The effect of aluminium was tested by passing a solution containing 50 mg Al_2O_3 and 50 gm Na_2CO_3 per liter through a one gram column. 500 ml of the effluent was collected which on analysis showed that all the aluminium passed out unadsorbed.

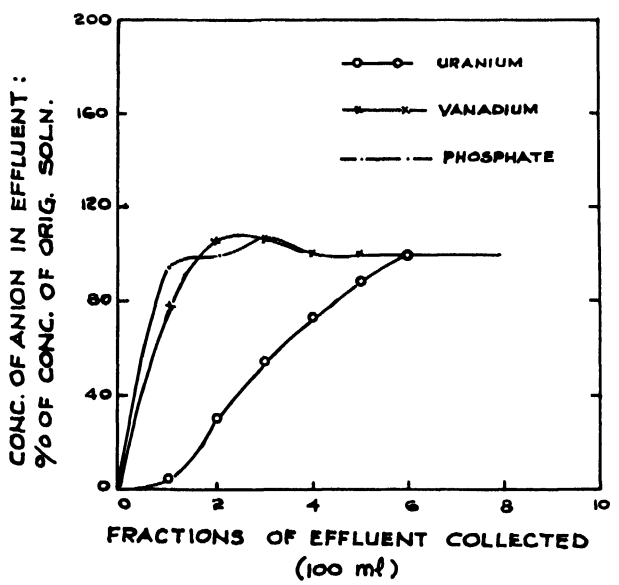

Figure 1. Adsorption from a mixture of uranyl tricarbonate, vanadate and phosphate

These studies thus showed that uranium while being adsorbed by the column from 5% Na_2CO_3 solution was simultaneously freed from such impurities like vanadium, phosphorus and aluminium. It might, however, be mentioned that in the absence of excess carbonate ions these anionic impurities would be taken up by the column just like any other anion.

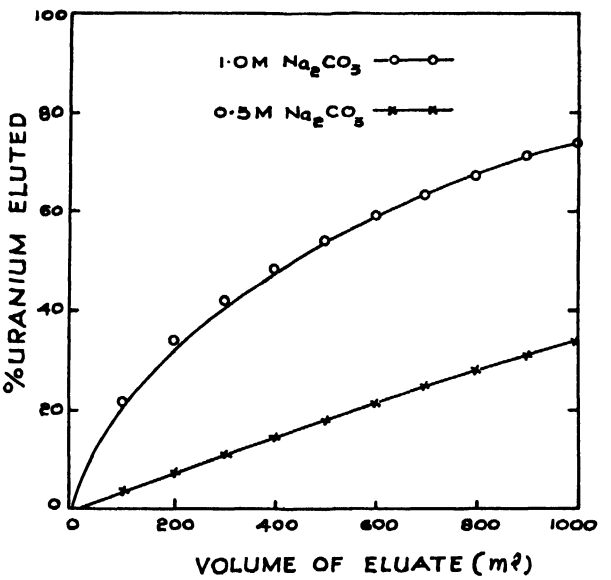

Figure 2. Elution of uranium with sodium carbonate

ELUTION OF ADSORBED URANIUM

Since uranium is adsorbed on the column as the complex anion $[UO_2(CO_3)_3]^{4-}$, an acid eluent is bound to liberate carbon dioxide resulting in breaking up of the column. Hence only neutral and alkaline eluting agents were tried. The efficiency of various reagents was compared using a number of one gram columns on each of which was adsorbed 50 mg uranium as carbonate complex. Elutions were carried out with solutions of known concentration at a speed of 50 ml per hour. 100 ml fractions of the eluate were collected and analysed for uranium.[5] The results are shown in Figs. 2, 3 and 4. As expected sodium carbonate proved to be inefficient (Fig. 2) for elution.

The behaviour of sodium hydroxide was different from that of either sodium chloride or nitrate. From Fig. 3 it is seen that the lower the concentration of NaOH the better did it elute while with all other eluting agents tried the reverse was the case (Fig. 4). In one experiment the elution was first carried out with *2M* sodium hydroxide till the eluate was free from uranium when it was found that only 50% of the uranium present in the column was eluted. Then the column was washed free from alkali and *2M* sodium chloride was used for eluting the uranium still held up in the column, but it was found that no more uranium was eluted though it was known from other experiments (Fig. 4) that this latter solution by itself could elute uranium completely

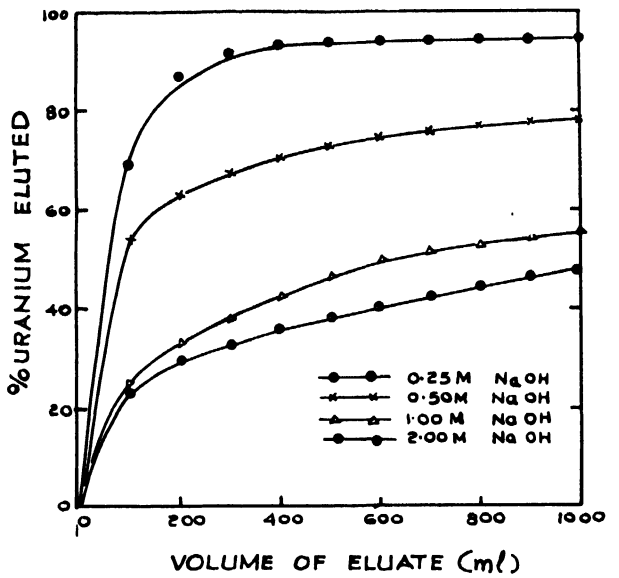

Figure 3. Elution of uranium with NaOH

from the column. However, on passing 2*N* hydrochloric acid the uranium held up was recovered. It was also observed that the eluate in case of NaOH was turbid and on standing deposited uranium in the form of a precipitate (most probably sodium diuranate). From these observations it was possible to explain the behaviour of sodium hydroxide in elution. Sodium hydroxide is known to precipitate uranium from the complex carbonate according to the equation

$$2[UO_2(CO_3)_3]^{4-} + 2Na^+ + 6OH^- \rightleftharpoons Na_2U_2O_7 + 6CO_3^= + 3H_2O$$

It is thus clear that uranium was converted from an anionic complex into an insoluble diuranate which partly passed out in the eluate and partly remained in the resin bed itself. Since the more dilute solutions of alkali precipitate uranium more slowly a greater part of it could pass out in the form of a colloidal suspension.

The behaviour of NaCl, $NaNO_3$ and Na_2SO_4 was normal in that the efficiency of elution increased with salt concentration. $SO_4^=$ ion, in spite of its higher valency, was less effective than either Cl^- or NO_3^- when solutions of same normality were compared.

These experiments thus showed that 2*M* sodium chloride or nitrate was the best suited, all the uranium being eluted with only 100 ml of the eluent.

ADSORPTION AND CONCENTRATION OF URANIUM USING 50 GM RESIN BEDS

In view of the encouraging results obtained in the preliminary experiments described above a more detailed study was undertaken using columns containing 50 gm resin. However, in these experiments the resin was taken in the nitrate form, chloride being eliminated for reasons given later in this report. The general procedure given below was used for these studies.

The column was prepared by converting resin equivalent to 50 gm oven dry resin chloride into the nitrate form in a tube, 23-mm diameter, by passing 10% $NaNO_3$ solution till the effluent was free from chloride. The column was washed with distilled water and the resin allowed to settle after back washing. Synthetic feed solution of known composition was then passed at a rate of 2 liters per hour (except in those experiments where the effect of flow rate on the break-through point was studied) until uranium appeared in the effluent and its concentration rose to a predetermined value. The tube was then rinsed free of excess uranium solution with distilled water at 2 liters per hour and the eluent was introduced at 200 ml per hour till the eluate was uranium free, followed by a water rinse at 500 ml per hour to remove excess nitrate. The column was then ready for a new cycle after a back wash.

In a series of experiments the following studies were made: (*A*) the effect of (1) feed flood rate and (2) feed composition on the capacity for uranium at the break-through point, and (*B*) the recovery and concentration of uranium in the eluate. In all the following experiments the break-through point was taken at 5% leakage,

$$\text{(i.e., when } \frac{\text{concentration of effluent}}{\text{concentration of influent}} \times 100 = 5\text{)}$$

THE EFFECT OF FEED FLOW RATE ON THE BREAK-THROUGH CAPACITY

Figure 5 shows the effect of feed flow rate on the break through capacity for uranium. It is seen that the capacity diminished rather sharply when the flow rate was increased beyond 50 ml per minute. There was, however, very little advantage in decreasing the flow rate below 30 ml per minute. Hence for

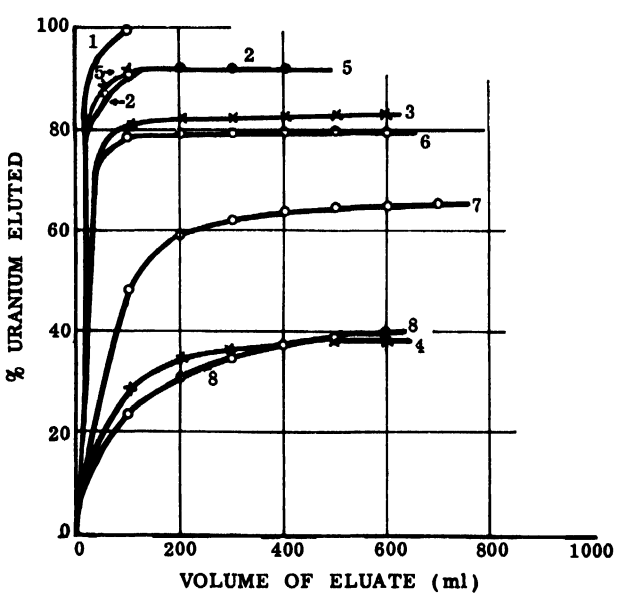

Figure 4. Elution of uranium; eluting solutions: (1) 2.0*M* NaCl; (2) 1.0*M* NaCl; (3) 0.5*M* NaCl; (4) 0.25*M* NaCl; (5) 1.0*M* $NaNO_3$; (6) 0.5*M* $NaNO_3$; (7) 0.5*M* Na_2SO_4; (8) 0.35*M* Na_2SO_4

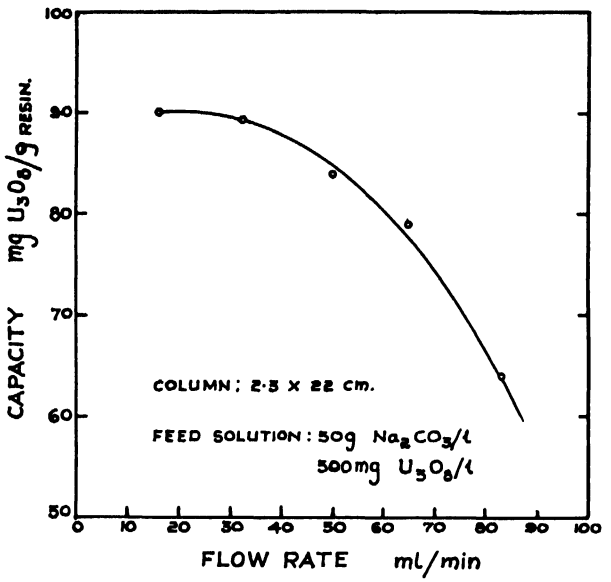

Figure 5. Effect of feed rate on break-through capacity for uranium

all further work a flow rate of 33 ml per minute or approximately 2 liters per hour was used.

EFFECT OF FEED COMPOSITION ON THE BREAK-THROUGH CAPACITY

The effect of the variation of sodium carbonate concentration was first studied. In the preliminary experiments it was found that the uranium uptake at equilibrium depended on the sodium carbonate concentration in the influent. In the operation of a column, however, the break-through capacity and not the saturation capacity is important. Feed solutions containing 500 mg U_3O_8 per liter (added as uranyl nitrate) and varying amounts of Na_2CO_3 were passed through 50 gm resin beds at a rate of 2 liters per hour. 500-ml fractions of the effluent were collected and analysed for uranium. The amount of uranium taken up by the column when 5% leakage occurred was determined in each run. The results are shown in Fig. 6 from which it can be seen that the capacity decreased with increasing Na_2CO_3 concentration. This point is of significance since the concentration of sodium carbonate employed for leaching varies from ore to ore (3–10% solutions are generally used).

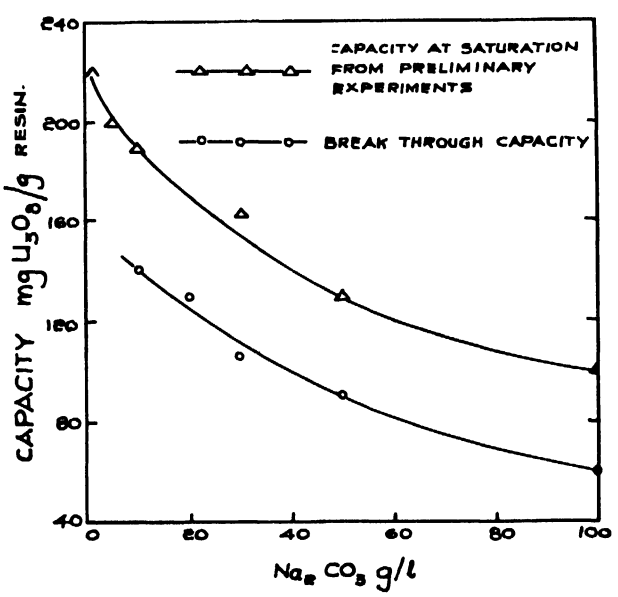

Figure 6. Effect of Na_2CO_3 conc. in feed on break-through capacity for uranium; feed flow rate: 33 ml/min; feed: 500 mg U_3O_8/l

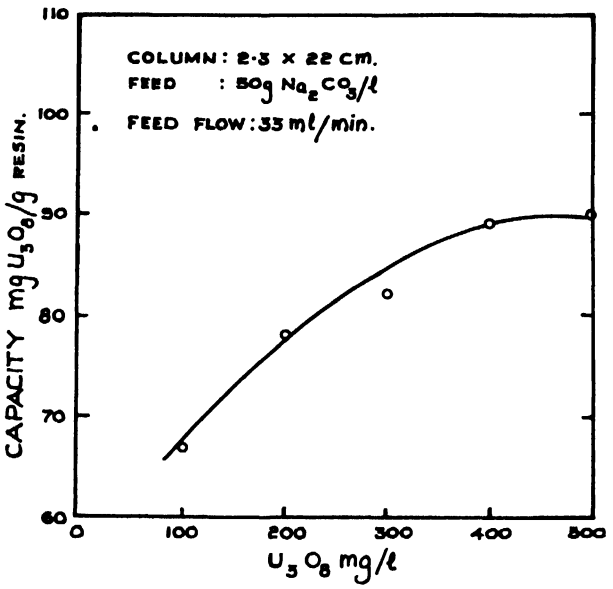

Figure 7. Effect of uranium conc. in feed on break-through capacity

VARIATION OF URANIUM CONCENTRATION

Since the concentration of uranium in the leach solutions can vary within wide limits depending on the grade of the ore treated, several experiments were done to find out the break-through capacity using feed solutions of different uranium concentrations. Figure 7 shows that the capacity decreased with decreasing uranium concentration indicating that a bigger column would be required to recover the same amount of uranium from a dilute solution than from a more concentrated one.

RECOVERY OF URANIUM FROM THE RESIN BED

From the results of the preliminary experiments it can be seen that NaCl or $NaNO_3$ in 1–2 molar solutions are effective eluting agents. It might, however, be mentioned that a dilute solution of NaOH (e.g., 0.25*M*) was also quite effective; but there is an inherent danger of part of the uranium being precipitated in the bed itself especially during the operation of bigger columns. Sodium nitrate was, however, preferred since the final recovery and purification of uranium from the concentrated eluates was proposed to be done by solvent extraction of uranyl nitrate where the presence of Cl ions is undesirable.

In a number of column runs during the course of this investigation attempts were made to recover ura-

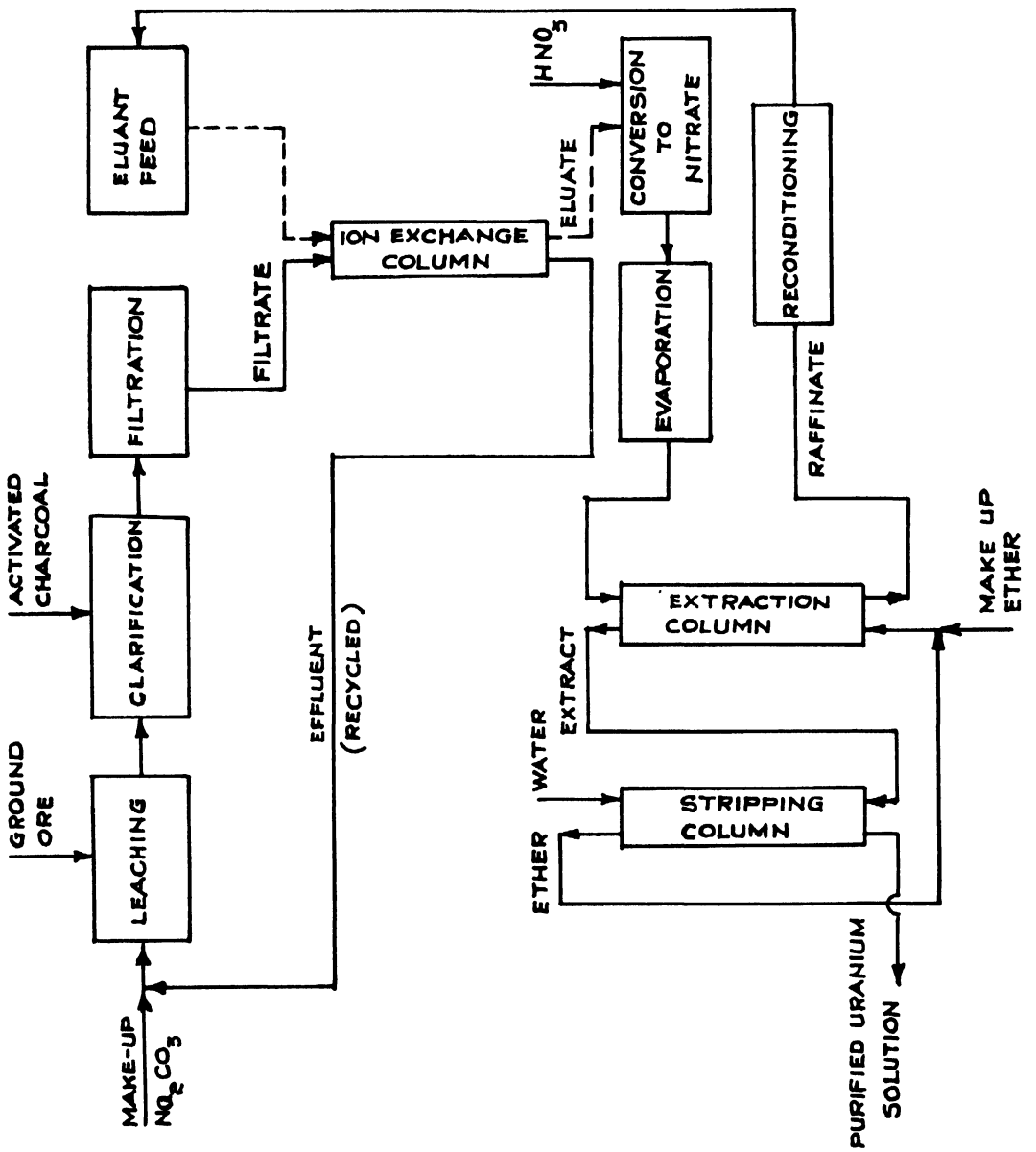

Figure 8. Proposed flow diagram for uranium extraction from low grade ore

nium with sodium nitrate and it was observed that while the recovery was on the whole satisfactory a small fraction (1–4%) of the adsorbed uranium was held up by the column. In an attempt to reduce this "hold back" it was found that the addition of a small quantity of sodium carbonate to the eluent was very effective for this purpose (Table II).

Table II. Elution of Uranium with Sodium Nitrate. Bed 2.3 × 22 cm, eluent volume 500 ml, rate 3.3 ml/minute

Run no.	Adsorbed uranium gm U_3O_8	Eluant	Per cent eluted
1	6.7	1.0 *M* $NaNO_3$	96.4
2	6.0	1.5 *M* $NaNO_3$	98.3
3	4.2	2.0 *M* $NaNO_3$	99.0
4	3.6	1.0 *M* $NaNO_3$ containing 5 gm Na_2CO_3/l	99.7
5	6.0	1.5 *M* $NaNO_3$ containing 5 gm Na_2CO_3/l	99.8
6	4.2	2.0 *M* $NaNO_3$ containing 5 gm Na_2CO_3/l	99.8

RECOVERY OF URANIUM FROM CARBONATE LEACH LIQUOR

A low grade ore assaying about 0.1% U_3O_8 on leaching with hot 5% soda ash solution gave a leach liquor containing 0.47 gm U_3O_8 per liter. This solution containing vanadium, phosphate and some organic matter was treated with activated charcoal to remove the organic matter and filtered. This was necessary since it was found that the organic matter was also taken up by the column and reduced its capacity for uranium. During the elution step this impurity was eluted along with uranium and continued to be eluted long after all the uranium had passed out. The clear pregnant solution was passed through a 50 gm resin column till the break-through point was reached, details of operation being the same as for synthetic solutions.

1.0*M* sodium nitrate solution containing 5 gm of sodium carbonate per liter was used for eluting out the uranium. The eluent was passed at a rate of 3.3 ml/minute and was collected in 50 ml fractions. The fractions were analysed for their uranium contents. The results of a typical elution test are shown in Table III.

Table III. Concentration of Uranium in the Eluate. Uranium Adsorbed on the Resin Bed = 3.92 gm U_3O_8

Eluate fraction no.	Uranium concentration gm U_3O_8/liter	Per cent uranium eluted
1	Nil	0
2	Nil	0
3–5	(Average) 26.0	99.8
6–10	(Average) 0.048	0.18

The results thus showed that 99.8 per cent of the adsorbed uranium could be eluted in the form of a solution containing 26 gm U_3O_8/liter (i.e., 55.5 times the uranium concentration in leach solution). While this represents the average concentration it was found that uranium in some fractions was as high as 65 gm/liter.

RECOVERY AND PURIFICATION OF URANIUM FROM THE ELUATE

Preliminary experiments showed that after acidifying and concentrating the eluate till sodium nitrate started crystallizing out, it was possible to separate most of the uranium in a pure form by extraction with diethyl ether. The raffinate after dilution and addition of requisite amount of Na_2CO_3 could be recycled for eluting uranium, thus economising on the use of $NaNO_3$.

The conventional sodium hydroxide method of precipitation could also be employed without any difficulty for recovering uranium from the eluate obtained above. The method described in this paper has the advantage of simultaneously purifying uranium and of utilising the sodium nitrate contained in the eluate as a salting-out agent. On the basis of the work described in this investigation a flow sheet (Fig. 8), for the recovery of uranium from carbonate leach liquors, is suggested. Pilot plant work, on the carbonate leaching of uranium from low grade ores or concentrates, as well as on its recovery by ion-exchange process from pregnant leach liquors, would be necessary before any assessment of the economics of the process could be made. It is, however, felt that no serious difficulty would be experienced in enlarging the scale of the process.

SUMMARY

An ion exchange process for the recovery and concentration of uranium from dilute solutions containing free sodium carbonate is described. Strongly basic resin, Amberlite IRA-400, was used for these studies. It was found that the uranium uptake depends on the feed composition. 1.0*M* sodium nitrate solution containing sodium carbonate was used for eluting the uranium from the resin bed and the concentration of uranium in the eluate was of the order of 25 gm/liter.

During the adsorption of uranium from a 5% Na_2CO_3 solution it was found that certain anions like vanadate, phosphate, aluminate etc., which are likely to be present in the plant leach liquors, pass out in the effluent. The recovery and purification of uranium from nitrate eluate could be achieved by ether extraction of uranyl nitrate.

The advantages of this method of recovering uranium are:

1. The effluent from the process can be recycled for contacting fresh ore.
2. In the adsorption stage uranium is freed from impurities like phosphate, vanadate, etc.
3. Sodium nitrate used for elution serves as a salting-out agent in solvent extraction process and the raffinate, after adjusting the composition, can be used for a second elution.

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Solvent Extraction of Uranium from Acid Leach Slurries and Solutions

By Robert R. Grinstead, K. Glenn Shaw, and Ray S. Long,* USA

Although the domestic uranium industry had its beginning many years ago, milling of uranium ore has always been accomplished by one of two hydrometallurgical methods. These are the acid leach and the carbonate leach processes, both of which include chemical precipitation from the leach solutions. Although the industry has been expanding rapidly since World War II, the nature of the known ore bodies is such that the same general methods are still required for dissolving uranium from the ore. However, several methods have been developed for treating the clarified leach liquors; these methods include improved precipitation processes and columnar ion exchange.

In view of the difficulties encountered with settling and filtration, the advantages to be gained by treating the leach pulp directly are obvious. Workers at the US AEC Raw Materials Laboratory† have approached this problem by using large bead ion exchange resins enclosed in a mesh cage. This process is in the pilot stage and is said to operate effectively. As a result of previous work done at the Dow laboratory on the solvent extraction of uranium from phosphoric acid, it was felt that the application of solvent extraction methods to the treatment of acid leach slurries would offer a fairly simple and economical solution to the problem. Such a process has been developed. Although it is applicable to a variety of uranium-bearing solutions, only the application to acid leaches of Colorado Plateau ores will be described in this paper. The process is being studied in a pilot plant located at the US Bureau of Mines Experiment Station in Salt Lake City, Utah, and operated jointly by personnel of that Station and of this laboratory.

PROCESS DESCRIPTION

A block diagram of the process is shown in Fig. 1. Operation is on a continuous basis up to the final precipitation. The crushing, grinding, and acid leaching circuit is conventional, the details depending upon the type of ore to be processed. The reduction step is optional and involves the addition of H_2S or other reducing agents to reduce ferric iron. Its inclusion in the flow sheet depends upon a number of factors, the chief one being the relative amounts of ferric iron and uranium present.

The extractant currently in use is a 0.1*M* solution of mono-(1-(2-methylpropyl)-3,5-dimethylhexyl) phosphate in kerosene (prepared from 2, 6, 8-trimethyl-4-nonanol).‡ This compound is also referred to as dodecyl phosphoric acid, or simply DDPA. From two to four stages of extraction are used, and recoveries of 99% or more of the uranium are obtained. The flow ratios are adjusted to produce an organic phase containing 6–8 grams U_3O_8/liter.

The uranium is stripped from the organic phase with 10*M* HCl. Although the equilibrium in the HCl system is very favorable, it is only slowly achieved. In spite of this, the use of three or four stripping stages will give tenfold concentrations from organic to HCl. Most of the HCl is recovered for further use by evaporation, and a final solution containing several hundred grams U_3O_8/liter is obtained. A concentrate is obtained from this solution by the conventional alkaline precipitation.

CHEMISTRY OF THE PROCESS

Leaching

This step has received little attention in this laboratory, but has been thoroughly studied by the workers at the US Bureau of Mines. Almost without exception acid leaches are made with H_2SO_4, in the presence of an oxidizing agent where needed, and the final solutions and slurries exhibit pH's in the range 0.5 to 1.5. Slurry densities during leaching range from 40% to 60% solids by weight. Originally it had been expected that the process would be applied to filtered solutions and desanded slurries. Both the filtering and the desanding operations involve some dilution with water so that the final solution concentrations are more dilute than in the leach pulp. To simplify the work, filtered solutions were used in the laboratory, and the range of composition of these solutions is shown in table on following page.

Desanded slurries were studied later in a countercurrent extractor. It has since been shown in the pilot plant that direct extraction of the leach pulp is possible; in this case, the solution concentrations may be up to four times those in the table.

*The Dow Chemical Company, Pittsburg, California.

† Located at Winchester, Massachusetts, and operated by the National Lead Company (formerly operated by the American Cyanamid Company).

‡ Carbide and Carbon Chemicals Corporation.

Species	*Conc., gm/l*
U_3O_8	0.7–1.7
V_2O_5	1–5
Fe	2–5
Al	3–6
$SO_4^=$	40–80
PO_4^{---}	0.2–1.4
Ti	0.01–0.1
Mo	<0.02
pH	0.7–1.2

Uranium and vanadium are nearly always present as the (VI) and the (IV) species, respectively, and iron occurs as a mixture of the (II) and (III) states. When reduction of iron is desired in order to prevent its extraction, commercial 50% NaHS solution and $Na_2S_2O_3$ are satisfactory reagents.

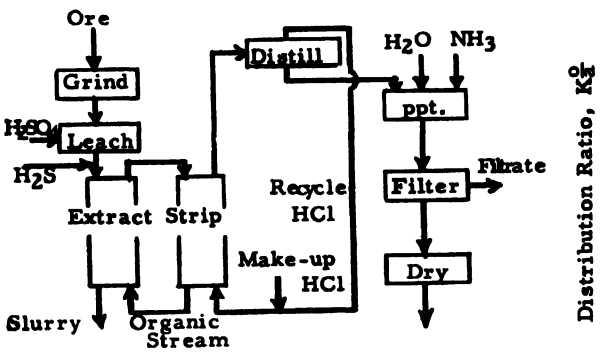

Figure 1. Block diagram of extraction process

Extraction Step

The compounds used as extractants were mono- and dialkyl-esters of phosphoric acid. Extraction evidently occurs according to reactions of the type:

$$2RH_2PO_4 + UO_2^{++} \rightarrow UO_2(RHPO_4)_2 + 2H^+ \quad (1)$$

$$2R_2HPO_4 + UO_2^{++} \rightarrow UO_2(R_2PO_4)_2 + 2H^+ \quad (2)$$

The only dialkyl ester studied, diisooctyl phosphate§ was quite insoluble in water but was precipitated by aluminum and could not be used. However, more recent work by the Raw Materials Section of Oak Ridge National Laboratory has shown that other dialkyl esters are free of this difficulty, and several of these compounds appear to be very promising extractants.

Monooctyl esters were too soluble in water, and esters containing longer-chain alkyl groups such as stearyl, cetyl and lauryl, gave formidable emulsions when contacted with aqueous systems. It was found however, that monoesters of long-chain alcohols containing the OH group near the center of the chain showed little tendency to emulsify and were fairly insoluble in water. In addition, the rate at which aluminum was extracted by the higher esters was much less than that with the octyl esters.

All of the monoalkyl phosphates were prepared in the laboratory by adding an approximately stoichiometric amount of the appropriate alcohol to a slurry of P_2O_5 in kerosene or other inert diluent. The principle reaction is believed to be

$$2ROH + P_2O_5 \rightarrow RO\text{–}\underset{\underset{OH}{|}}{\overset{\uparrow}{P}}\text{–}O\text{–}\underset{\underset{OH}{|}}{\overset{\uparrow}{P}}\text{–}OR \quad (3)$$

(O above each P)

The resulting clear solution was refluxed for about one hour with 1*N* HCl to hydrolyze the pyrophosphate ester to orthophosphates. A yield of about 70% of the monoester was usually obtained. A series of these esters, prepared as 0.5 *M* xylene solutions, was compared on a number of points.

Extraction of uranium(VI), vanadium(IV), iron (II), and aluminum ions by the esters and tendencies toward emulsification were compared by contacting them with samples of a leach solution. Losses of esters to aqueous phases were examined by contact with aqueous sulfate solutions of pH 1.2. These results are given in Table I.

There is a marked decrease in loss of ester to the aqueous phase with increasing chain length. Low emulsifying tendencies seem to be more the result of the branching in the chain than of the chain length. Uranium and vanadium distribution ratios appear to increase generally with chain length; those for ferrous iron show no very clear trend, and those for aluminum appear to decrease. Actually, the trends are mainly a result of the fact that the rate of extraction of aluminum is slower than that for uranium and, in addition, decreases greatly as the alkyl chain length increases. The data in the table were obtained for a one-minute contact, at which time the octyl ester systems are close to equilibrium. However, the longer-chain ester systems require two or three hours to achieve equilibrium with respect to aluminum. With a one-minute contact, therefore, relatively little interference due to extraction of aluminum is observed.

The equilibrium distribution ratio for aluminum actually does decrease as the alkyl chain length increases, but the spread is only about a factor of two at equilibrium instead of the fortyfold difference shown in the table. As a result of this slow aluminum extraction the distribution ratios for uranium will drop somewhat with continued contact, although the drop is not serious. In Fig. 2 is shown the distribution ratio for uranium as a function of time in two experiments involving solutions of uranyl sulfate, sodium sulfate, sulfuric acid and aluminum sulfate in contact with 0.1*M* DDPA. With aluminum absent, extraction of uranium was rapid. With an initial aqueous concentration of 6.7 grams Al/liter, the initial uranium extraction was rapid but not as complete, and the distribution ratio gradually fell to a value of about 200 after four hours. The final organic and aqueous concentrations of uranium were about 1 gram U_3O_8/liter and 5 mg U_3O_8/liter, respectively, indicating a point on the distribution curve close to the origin.

§ Victor Chemical Company.

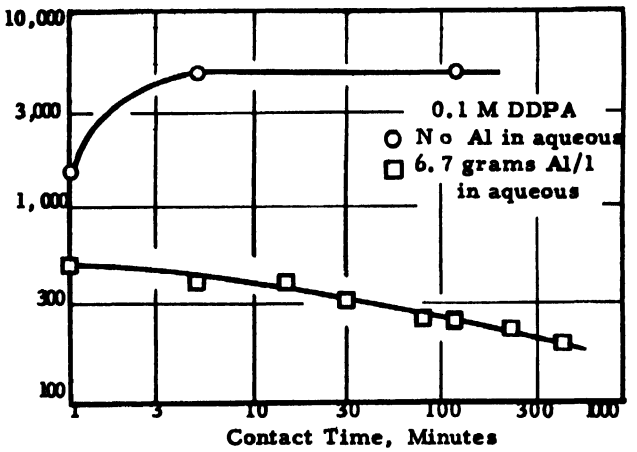

Figure 2. Effect of Al on extraction of uranium

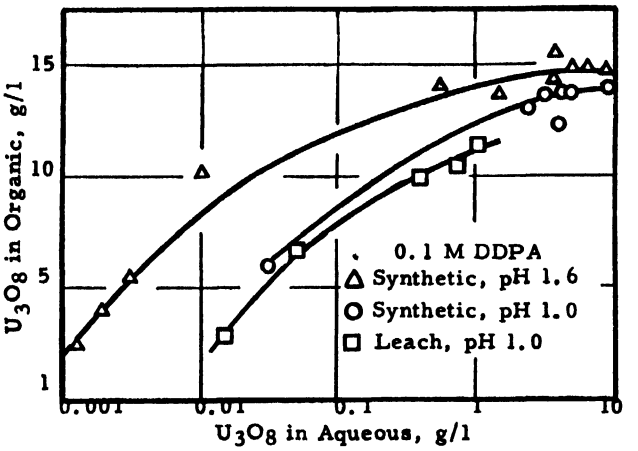

Figure 3. Uranium distribution ratios

In Fig. 3 are presented three distribution curves for uranium in similar systems. It is evident that the distribution ratio increases with increasing pH. The deleterious effect of the aluminum, even at one minute contact time, is also evident. However, the concentration of aluminum in the organic is not high, and contamination of the uranium product is not serious. In the experiment shown in Fig. 2 the aluminum content of the organic was only 0.7 gram Al/liter after two hours.

Ferric iron is extensively extracted, and exhibits a distribution ratio of the same order of magnitude as that of uranium. When the amount of iron is not sufficient to reduce seriously the capacity of the extractant for uranium, reduction to the ferrous state is not required. However, since the distribution ratios for uranium and iron are comparable, the extraction of one is greatly influenced by the presence of the other, and it is not possible to obtain a simple answer as to how much ferric iron can be tolerated. Although vanadium and ferrous iron are not strongly extracted, the situation is similar. The levels of these species in the organic phase will depend upon how nearly the extractant is saturated with the more strongly extracted species. This problem has been most easily studied in a laboratory-size, continuous, countercurrent extractor where plant conditions are closely simulated.

Such a unit was built and operated in the laboratory. Three or four extraction stages were used and the same number of stripping stages. The operating range of the unit was 20–30 ml leach solution per minute. Data obtained from six runs are shown in Table II.

In all of these runs at least 95% recovery of uranium was obtained. Essentially complete removal of the uranium, vanadium, and iron from the organic was achieved with 10*M* HCl strip. It can be seen that the extraction of vanadium is favored not only by high pH values, but also by low flow ratios, which leave more extractant available for the vanadium.

Stripping of Uranium from Organic Phase

According to the equation for uranium extraction, any strong acid should tend to reverse the equilibrium

Table I

Alcohol used in preparation	*Distribution loss to aqueous phase, grams ester/liter*	*Phase separation time with USBM-2, sec*	*Distribution ratio*, $K_{o/a}$ with USBM-2 contact time = one min*			
			U_3O_8	V_2O_5	*Al*	*Fe(II)*
n-octanol	1.0	>24 hours	—	—	—	—
2-octanol	1.4	100 sec	250	2.3	—	0.05
2-ethyl hexanol	3.0	105 sec	230	2.1	1.6	0.10
3, 3, 5-trimethyl cyclohexanol	1.6	25 sec	230	1.7	0.90	0.12
2, 6-dimethyl-4-heptanol	1.1	25 sec	570	1.5	1.1	0.10
dodecanol†	0.10	25 sec	520	5.5	0.17	0.06
2-butyloctanol	0.065	80 sec	740	2.8	0.43	0.09
tetradecanol‡	0.05	30 sec	1420	5.6	0.12	0.05
heptadecanol§	0.003	40 sec	800	18.6	0.04	0.04

* $K_{o/a}$ = Concentration in organic/concentration in aqueous. U values measured at aqueous : organic ratio of 5 :1 and others at 1 :1.

† 2, 6, 8, -trimethyl-4-nonanol.
‡ 2-methyl, 7-ethyl-4-undecanol.
§ 3, 9-diethyl-6-tridecanol.

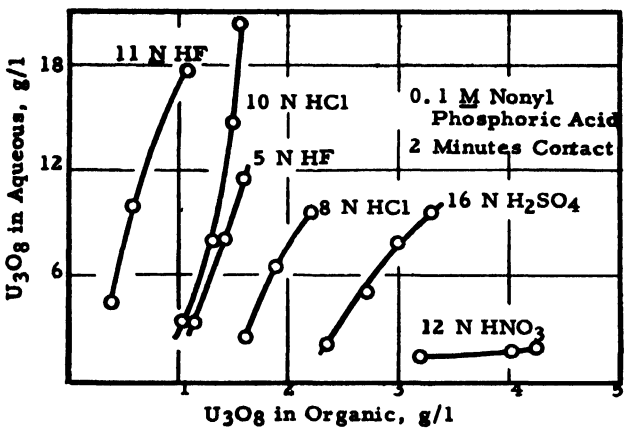

Figure 4. Mineral acids for uranium stripping

and be a potential stripping reagent. Mineral acids, therefore, have been the usual stripping agents employed for the monoalkyl phosphates. Carbonate and other bases are not satisfactory because of both the solubility of the disodium alkyl phosphate in the basic solution and the insolubility of the salt in kerosene. In Fig. 4 various concentrations of mineral acids are compared as stripping agents for mono-[1(2-methylpropyl)-3-methylbutyl] phosphate (nonyl phosphoric acid, or NPA). The most effective acids are those which complex uranyl ion and thereby shift the equilibrium toward the aqueous phase. The contact time of two minutes used here is not sufficient to achieve equilibrium, but for a given contact time the actual effectiveness of the various solutions would be expected to be in the order shown.

Because of the relative ease of recovering excess HCl by evaporation for recycle, coupled with reasonable cost and favorable distribution ratios, this acid has been used almost exclusively. The optimum concentration of HCl was found to be about 10*M*. Although distribution ratios are higher with more concentrated HCl, hydrolysis rates of the esters, which are negligible when in contact with 10*M* HCl, increase rather rapidly above this point.

The rate at which uranium is stripped into HCl is slow. This is illustrated by Fig. 5, where distribution curves are plotted with time as a parameter. Vanadium, both ferrous and ferric iron, and molybdenum are rapidly stripped from the extractant. Aluminum is stripped slowly, but sufficiently to prevent excessive build-up. Titanium is not stripped, but can be removed with 5% HF or an equivalent molar concentration of NH_4F.

Recovery of Uranium from Strip Solutions

Little difficulty is encountered in obtaining a high-grade concentrate from the HCl solution. In actual operation it has been found that a fairly good balance between evaporation cost and HCl loss is struck if the solution is evaporated to a uranium concentration of about 500 grams U_3O_8/liter. This solution is diluted with water and neutralized with ammonia. The precipitated uranium is filtered, washed free of chloride, dried, and calcined. In the presence of molybdenum, a NaOH wash may be required to produce a specification-grade concentrate.

SLURRY EXTRACTION EQUIPMENT

The process has been successfully operated for extracting uranium from clarified liquors and acid leach slurries of a variety of Colorado Plateau ores. The slurries treated ranged from desanded pulps containing five per cent solids to high-density slurries of sixty per cent solids. The extractant used in all of these studies was a 0.1*M* solution of mono-[1-2-methylpropyl)-3,5-dimethylhexyl] phosphate in-kerosene. The types of slurry feeds and the extraction equipment were compared on the basis of uranium recovered and the amount of organic mechanically entrained in the slurry phase.

Three different types of extraction equipment were used to process this range of slurry feeds, but the principles of contacting and settling remained the same. The extraction system was comprised of a number of stages. Each stage consisted of a mixing device and a settling chamber. The mixing device forced intimate contact of the two immiscible phases, permitting mass transfer of the uranium from the slurry phase to the organic. In order to prevent emulsification of the two phases, it was mandatory to maintain the organic phase continuous while mixing, i.e., to disperse the droplets of slurry within the organic phase. This condition was maintained, even though the slurry flow rate exceeded that of the

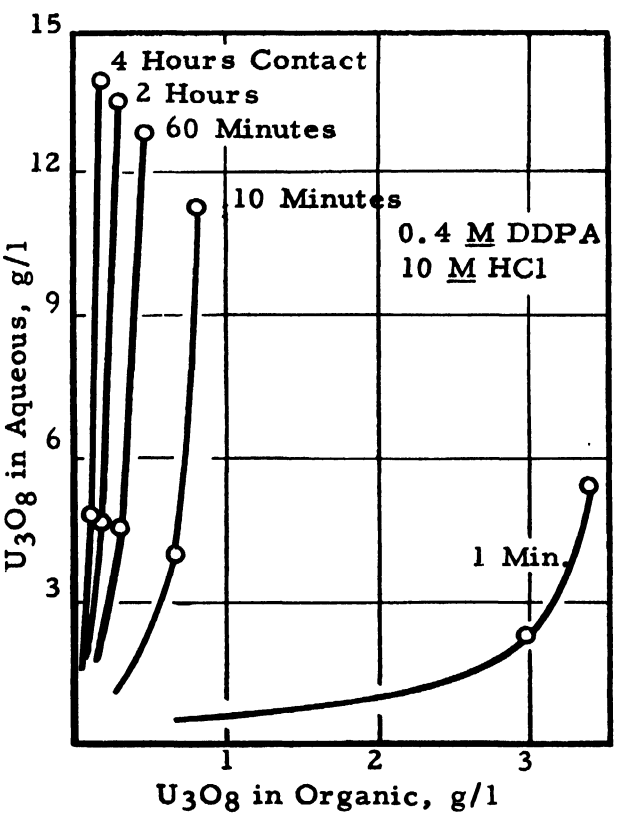

Figure 5. Effect of time in strip

organic, by returning the bulk of the contacted organic from the settler to the mixer. Gravity separation of the two phases followed the mixing step. A distinct interface marked the boundary between the lighter organic phase on top and the heavier slurry phase on the bottom.

Description of the Equipment

Three extraction devices were found most successful in contacting the acid slurries and the organic extractant. These were the conventional mixer-settler, the pump-mixer, and the internal mixer-settler.

The conventional mixer-settler is shown in Fig. 6. The mixer was a baffled tank agitated by a motor-driven turbine impeller. The settler was a quiescent tank of similar size. The mixed phases flowed to the settler through the lower transfer line and the recycle organic was returned to the mixer through the upper transfer line. The contacted aqueous then flowed by gravity through the external overflow leg. The solvent phase overflowed through an opening near the top of the settler. The mixer-settler stages were arranged in a cascade permitting gravity interstage flow of one phase, but necessitating interstage pumps for transfer of the other.

The pump-mix extractor was a modification of the mixer-settler. An external centrifugal pump was substituted for the baffled mixing tank. This device is shown in Fig. 7. The slurry and organic were fed into the pump with the recycle organic stream. After providing residence time of a few seconds, the mixture was pumped into the settling tank. Phase separation occurred at the interface in the lower section of the settler. The aqueous and organic phases flowed by gravity to the next stages. This system required no interstage pumps other than the mixing pumps.

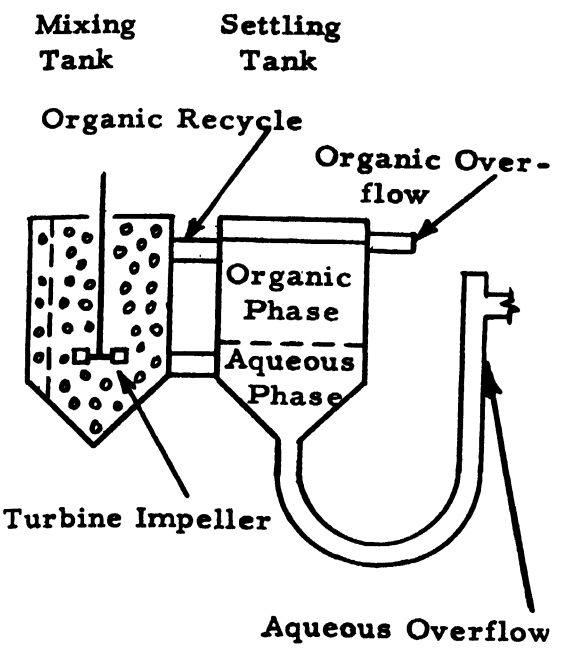

Figure 6. Mixer-settler

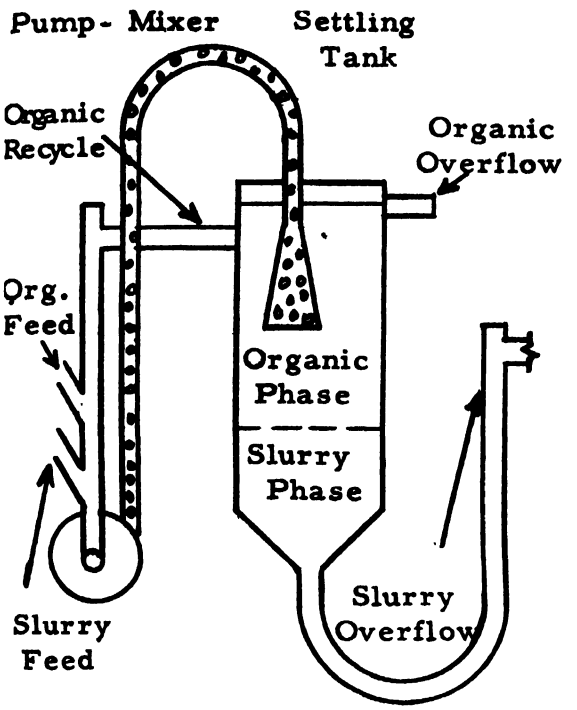

Figure 7. Pump-mixer

The internal mixer-settler was a contactor which combined the mixer and settler in one tank. This device is shown in Fig. 8. A shrouded turbine impeller was located in the lighter, organic phase. The slurry and organic were fed to this impeller through a well surrounding the shaft. Recycle organic was drawn into the mixing blade from above and below, thereby

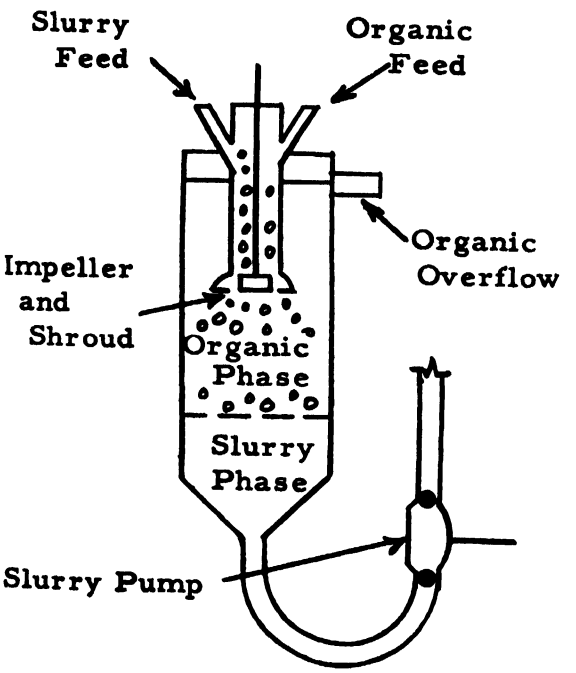

Figure 8. Internal mixer-settler

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Table II. Extractant: 0.1M DDPA-Kerosene. Fe^{+++} Completely Reduced in all Runs

Solution	pH	Conc. of species, gm/l				Flow Ratio	Weight ratio in product		
		U_3O_8	V_2O_5	Fe	Al	Aq.:Org.	U_3O_8	V_2O_5	Fe
Lukachukai (USBM-2)	1.0	1.2	3.4	3.4	4.7	5:1	100	6.2	0.9*
Temple mountain	1.3	1.2	4.0	5.6	5.7	5:1	100	20	1.4
Vitro	1.2	1.4	1.4	2.1	3.5	4:1	100	4.3	1.4
Slick rock	1.0						100	4.2	1.9
Slick rock	1.3	0.7	4.6	1.9	4.5	6:1	100	11.7	0.9
Slick rock	1.6						100	11.0	1.7

*U_3O_8:Al = 100:1.6.

Table III

Feed	Contactor	Stages	U_3O_8 recovery	Entrainment*
Clear liquor	Mixer-settler	4	99	Nil
	Pump-mixer	1	95	Nil
	Internal mixer-settler	—	—	—
Desanded slurries 5–15% solids	Mixer-settler	1	96–97	1.3%
	Pump-mixer	1	98	2%
	Internal mixer-settler	1	98	0.6%
High density slurries 48–60% solids	Mixer-settler	—	—	—
	Pump-mixer	1	95	10–12%
		2	98–99	10–18%
	Internal mixer-settler	1	86†	1–4
		2	89–95†	2–4
		4	97	5–7

*Entrainment = Vol. of solvent in raffinate/Vol. of raffinate. †Oxidized solutions.

maintaining the organic phase continuous. Separation of the phases occurred at the interface located well below the impeller. The stages were arranged in a cascade with interstage flow of the organic by gravity, and transfer of the slurry by pumps.

Performance of the Equipment

Performance of these extractors in the pilot plant depended on the type of feed. Operation was begun using clarified liquors and conventional mixer-settlers. Following this, runs were made treating first, desanded slurries, and finally, high density slurries. A summary of the results of these studies is presented in Table III.

No process difficulties were encountered in treating clear liquors. Attempts to use the mixer-settler for treating desanded slurries were not satisfactory. Control of the organic-to-aqueous mixing ratio was difficult and frequently emulsions formed.

Successful extractions of both desanded and high density slurries were made using the pump-mixer and the internal mixer-settler. However, it was necessary to maintain a high organic-to-aqueous mixing ratio (>50) to prevent emulsion formation. Recoveries using either contactor were comparable, but use of the pump-mixer resulted in higher loss of solvent as entrainment.

A settling tank was introduced after the last stage for reducing entrainment in the raffinate. A residence time of several hours was sufficient to float this solvent when treating desanded slurries. However, the high density slurries had to be first diluted with water to release the mechanically-held organic droplets. Usually about 90 per cent of this organic could be returned to the extraction system.

ACKNOWLEDGEMENTS

The authors gladly acknowledge the assistance of Mr. J. E. Magner and Mrs. R. L. Mason in carrying out much of the experimental work, and of the analytical section under Mr. H. O. Kerlinger and Mr. M. D. Yeaman in performing the analysis.

Recovery of Uranium from Phosphates by Solvent Extraction

By Ray S. Long, David A. Ellis, and Richard H. Bailes,* USA

The phosphate rock mined in Florida and the western states contains an average of 0.01% U_3O_8. While this is a relatively small concentration, it represents a large supply of uranium when total production of phosphate rock is considered. Since the mining and processing of the ore is financed by existing fertilizer production, the cost of by-product uranium recovery is not as high as might be expected.

Most of the domestic phosphate mined is used in the manufacture of ordinary and triple superphosphate fertilizers. In triple superphosphate manufacture, early work indicated that, in the initial acidulation, about 70% to 90% of the uranium in the rock is solubilized by the H_2SO_4 and reports into the commercial H_3PO_4 intermediate thus formed. The resulting solution contains about 90 to 200 mg U_3O_8/liter. Since uranium can be removed most economically at this point in the process, a large portion of the work has been done on these solutions. However, a preliminary study has been made of an alternative process for recovery of uranium from the solid superphosphate product.

The phosphoric acid solutions have the following approximate analysis: U_3O_8, 90–200 mg/liter; Fe, 4–6 grams/liter; Al, 3–5 grams/liter; PO_4, 300–600 grams/liter; SO_4, 30–60 grams/liter; F, 10–20 grams/liter; Si, 2–4 grams/liter; sp. gr., 1.3; and EMF, 240 to 300 mv.

The potential given was measured with a platinum and a saturated calomel electrode (S.C.E.). The EMF value indicates the potential of the calomel electrode with respect to the platinum so that a more positive potential denotes a more highly reduced solution.

RECOVERY FROM PHOSPHORIC ACID

The process for recovery of uranium from phosphoric acid consists of: (1) contacting the acid with a 1–2% solution of an alkyl pyrophosphate in kerosene; (2) separating the phases; (3) recovering the uranium from the solvent as a fluoride salt by precipitation with 48% HF; (4) re-using the solvent on a continuous basis with a required amount of fresh solvent make-up.

A simplified flow diagram is shown in Fig. 1. Analyses of the phosphoric acid leaving the extraction system indicate that it is relatively unchanged except in uranium content.

Extractant Preparation

The alkyl pyrophosphates have a high selectivity for uranium over various contaminants. Pyrophosphates with relatively long-chain alkyl groups are virtually insoluble in water but completely miscible in hydrocarbon diluents such as kerosene. Compounds made with alcohols ranging from 4 to 17 carbons have been tested. The extracting power per mole of ester increases with increasing chain length up to 12 carbons but, for economic reasons, octyl esters have been used most extensively. Capryl alcohol (2-octanol) is preferred for preparation of the ester because of the low cost.

Octyl pyrophosphoric acid (OPPA) is available commercially. However, since these compounds hydrolyze to orthophosphates in time, it is recommended that the material be made in the laboratory within a few days before usage. The hydrolyzed products are less effective extractants by a factor of about tenfold. Thus, a 10–20% solution of octyl orthophosphoric acid (OPA) is required for uranium recovery comparable to that obtained with 1% to 2% OPPA. A commercial OPA is available, also. This product consists of a mixture of mono- and dioctyl orthophosphates. The extraction of uranium from phosphoric acid was studied with both OPPA and OPA solutions.

The OPPA solvent is prepared by the following reaction;

$$2C_8H_{17}OH + P_2O_5 \rightarrow C_8H_{17}O\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{|}}{P}}OC_8H_{17} \quad (1)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad H \qquad H$$

Since the reaction is exothermic, the operation is best carried out in the presence of sufficient kerosene to limit the maximum temperature reached to about 70°C. This can be achieved by use of about one liter of kerosene per mole of P_2O_5. Best yields are obtained if the P_2O_5 is slurried in the kerosene first and the alcohol then added. The reaction is complete after about 30 minutes.

The material thus prepared is diluted to 1% to 2% with kerosene. The purpose of the kerosene diluent is to lower the viscosity of the solution, thus

* The Dow Chemical Company, Pittsburg, California.

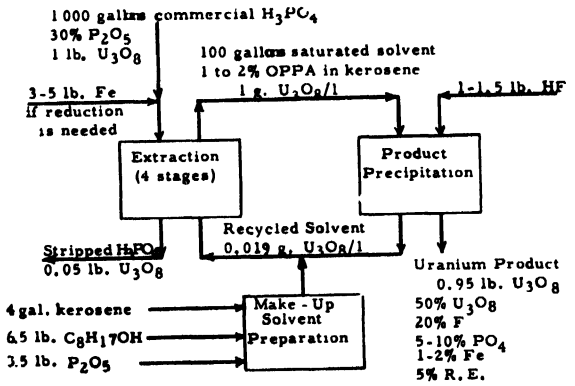

Figure 1. Flow diagram for extraction of uranium from phosphoric acid

reducing the tendency to emulsify when it is mixed with phosphoric acid. Other common diluents can be used. The choice of diluent has little effect on the resulting extraction.

The distribution or solubility loss of OPA into 30% H_3PO_4 from kerosene is about 0.004 grams/liter at 25°C and about 0.03 grams/liter at 50°C. The solubility loss of OPPA is of about the same magnitude.

Factors Influencing Extraction from the Acid

The extraction of uranium from phosphoric acid with alkyl pyrophosphates is believed to proceed according to a reaction of the following type:

$$2R_2P_2O_7H_2 + U^{++++} \rightarrow (R_2P_2O_7)_2U + 4H^+ \quad (2)$$

It is probable that a six-membered chelate ring is formed between the uranous ion and the P-O-P linkage.

Oxidation State

There is evidence that ions of higher positive charge are more highly extracted by the solvent. Thus, the extraction of uranium is greatly improved by reduction of the solution which forms U^{++++} from UO_2^{++}. Iron, which is a major contaminant, is also reduced from the highly extracted ferric state to the poorly extracted ferrous state. Most commercial H_3PO_4 has an EMF of −240 to −300 mv. In this range, maximum extraction coefficients (ratio of concentration of U_3O_8 in organic to concentration of U_3O_8 in aqueous phase) of about 10–15 are found with 2% OPPA. If the solution is reduced (0 to +100 mv), the coefficient it increased to about 200 (see Fig. 2). Because the maximum amount of uranium that can be extracted is limited by the amount of extractant present, the value of the extraction coefficient drops as the concentration of uranium in the organic increases.

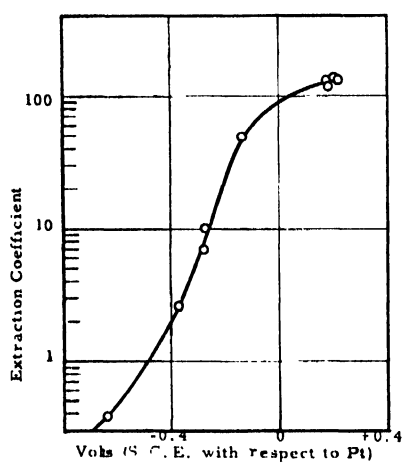

Figure 2. Extraction of uranium from H_3PO_4 with 1% OPPA in kerosene—effect of reduction

It has been found that the solution can be reduced most economically with scrap iron. The solution can be contacted with the iron either in a batchwise manner or continuously in a column. About 4 grams Fe/liter is generally required for complete reduction. Reduction is needed only if the EMF is more negative than −300 mv.

Phosphate Concentration

The OPA extraction coefficient is adversely affected by increasing phosphate concentration. The coefficient varies with the inverse fourth power of the phosphate concentration. With OPPA, a smaller effect of phosphate was noted. Since phosphate appears to inhibit uranium extraction, it is better in most plants, to operate on acid prior to evaporation.

Temperature

The extraction coefficient at 50°C is only about 30% of that obtained at 25°C with either OPA or OPPA.

Fluorides

The presence of uncomplexed fluoride lowers the extraction. This can be offset by addition, if desired, of small amounts of silica which ties up the fluoride and thus increases the value of the extraction coefficient.

Physical Factors

Any desired degree of extraction can be obtained by proper adjustment of such operating factors as concentration of OPPA in diluent, feed ratio of solvent to acid, and number of stages used in the extraction. Increasing any of these increases the extraction.

Countercurrent Extractions

Although several types of contactors can be used, most of the countercurrent experiments were done with mixer-settlers. Mixer-settlers give higher stage efficiencies than other types of extraction equipment, and recovery of the solvent for further treatment is simple. In a four-stage, countercurrent mixer-settler at a 10:1 flow rate ratio of aqueous to organic, 2% OPPA was required for 90% recovery of uranium from unreduced feed acid, but only 1% OPPA was required for the same recovery from reduced acid. When 10% OPA was used, 90% of the uranium was extracted from reduced acid at a 16:1 ratio of aqueous to organic. These extractions were obtained on acid

containing about 30% P_2O_5. About five minutes of mixing time and five minutes of settling time were employed in each stage. Higher extractions can be obtained by using larger amounts of extractant. When about five minutes of settling time and a one-ft² settling area per gallon per minute of feed rate were employed in the last stage, it was found that about 1% to 3% of the feed organic was entrained in the outgoing acid. A feedback of organic from the settler into the mixer in the final stage to maintain the condition of organic phase continuous during mixing lowered this entrainment to about 0.6%. Entrainment is lowered by increasing the ratio of organic to aqueous during mixing.

Precipitation of Product from Extractant

The uranium can be precipitated almost quantitatively from the OPPA by contacting it with about 1 to 1½ lb HF/lb of U_3O_8. The HF is best applied as a 48% to 60% solution. Higher concentration results in excessive deterioration of the solvent. Lower concentration causes emulsion. Contact time need be no greater than 15 seconds.

The following reaction appears to take place:

$$(R_2P_2O_7)_2U + 4HF \rightarrow UF_4 + 2R_2P_2O_7H_2$$

(Partially hydrolyzed to-RPO_4H_2) (3)

The product thus obtained is a uranous fluoride containing about 50% U_3O_8 with fluoride, phosphate and iron the major contaminants. Some phosphoric acids contain small amounts of rare earths. These are extracted with the uranium and result in cakes containing about 5% rare earth oxides.

Restoration of the Extractant

The HF partially hydrolyzes the pyrophosphate and reacts to some extent with orthophosphates. For OPPA, a two-minute contact with HF lowers the extraction coefficient to ¼ its original value and an eighteen hour contact to 1/40 of its original value. In order to restore the organic to its original extracting ability, a make-up of 50% to 100% of the original amount of OPPA used is required depending on the conditions of extraction and stripping. With continued usage, it appears that the extraction is due to both the OPPA and the OPA components. The latter is present because of decomposition of the former. The make-up quantity required is of the order of 3 to 10 lb of OPPA per lb of U_3O_8. Other raw materials required in this process per lb of U_3O_8 are 1.25 lb HF, 3 to 4 gallons of kerosene, and, in some cases, about 3 to 5 lb Fe.

Economics and Application of Process

The process for uranium recovery from H_3PO_4 as outlined has been investigated extensively in the laboratory. Acids from about twelve different commercial sources have been tested but no significant difference was noted. The laboratory work was followed by pilot plant testing. Several full-scale plants using this process are either now in operation or planned. Cost estimates have shown that the uranium produced from H_3PO_4 by this procedure is competitive with that from medium-grade ores (0.1 to 0.3% U_3O_8) if the ore is mined solely for uranium. Size of the phosphate plant is the most critical factor in determining the final cost.

RECOVERY FROM NORMAL SUPERPHOSPHATE

In the manufacture of normal superphosphate, less H_2SO_4 per ton of ore is employed than in the phosphoric acid process. The acid is pugged wih the ore and the resulting mass is allowed to cure prior to bagging. At no point in this process does the uranium appear in solution. However, a process for recovering up to 80% of the uranium from the final superphosphate product has been studied on a laboratory basis. This process consists of: (1) adding 6 lb HNO_3/ton of ore to the original acidulation step in manufacture of the superphosphate; (2) extracting the uranium from the superphosphate after "setting up" by a percolation leach with a 1% to 2% solution of OPPA in hexane at about a 1 : 1 ratio of organic to ore; (3) washing entrained OPPA from the solids with fresh hexane; (4) recovering the hexane by heating the solids to a temperature not greater than 80°C; (5) stripping the uranium from the loaded OPPA.

Hexane is used because its low boiling point (69°C) makes it recoverable by boiling at a temperature sufficiently low so that there is no danger of reversion in the superphosphate.

The uranium can be stripped from the solvent with HF, HCl, aqueous polyphosphates, or other reagents studied in the phosphoric acid investigation. The solvent is then recycled after make-up addition of OPPA to compensate for loss of extracting power incurred during stripping.

In the superphosphate preparation, the variables whch affect uranium recovery are the amount of H_2SO_4 used, the amount of HNO_3 added per ton of ore, and the time of aging after acidulation. In general, an increase in any of these will increase the extraction. The variables in the extraction procedure which affect uranium extraction include concentration of OPPA in the solvent, ratio of organic to solid used during extraction, time of contact, and number of stages or contacts employed. Increasing any of these variables increases the extraction. Decrease in particle size of the superphosphate product also increases the extraction.

Superphosphate after being treated by this procedure was found to have the same weight and P_2O_5 analysis as before treatment. However, no agronomic tests have been run on any of the material.

Laboratory results have indicated that a similar process might be applied to triple superphosphate. The advantage of this over extraction of the H_3PO_4 intermediate lies in the 30–40% additional uranium

which might be available. Pilot plant testing on these processes is believed necessary.

In summary, solvent extraction processes employing alkyl ortho- and pyrophosphates have been developed for byproduct recovery of uranium from H_3PO_4 and superphosphate. The former process has received both laboratory and pilot plant development. It has been installed in full scale plants and has been found to produce uranium at a cost competitive with higher grade sources.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Mr. Herbert O. Kerlinger and Mr. M. Dean Yeaman for their help in the analytical problems encountered in this project.

Canadian Practice in Ore Dressing and Extractive Metallurgy of Uranium

By A. Thunaes,* Canada

The uranium ores that are being treated today in Canada do not contain other values in sufficient amounts to warrant their recovery.

Other potentially important mines that are scheduled for operation in 1955 or 1956 do not differ in this respect. The uranium must pay for the entire cost of development, mining and milling.

The treatment plants that are now in operation are located in the Arctic or sub-Arctic area of the Northwest but the Province of Ontario is expected to become a major producer in the next two years.

The following outline deals with the methods that are employed in Canada for recovery of uranium from original ores in a product that is suitable for refinery feed.

URANIUM MINERALS AND ASSOCIATED MINERALS IN THE MORE IMPORTANT CANADIAN ORES AND THE EFFECT OF THESE MINERALS ON ORE TREATMENT

Pitchblende is the principal source of uranium in the mines that are currently producing in Canada; however, several mines that are now planning or approaching the production stage contain Brannerite or uranothorite, major uranium bearing minerals.

Pitchblende ores vary considerably as regards treatment characteristics. Thus, the ore in the Port Radium mine contains a considerable amount of heavy pitchblende in seams and veins, and up to 70% recovery of uranium was formerly obtained by gravity concentration.[1] On the other hand, the ores of the Beaverlodge area contain finely disseminated pitchblende of lesser specific gravity and even after fine grinding the pitchblende grains will generally contain gangue minerals.

The minimum content of U_3O_8 in acceptable refinery feed is 10%; even when the ore contains considerable massive and heavy pitchblende, as in the Port Radium area, the per cent recovery by physical methods is not acceptable today.

Consequently, hydrometallurgical methods are essential to efficient recovery.[2] The two principal methods that have been developed or modified for Canadian plants are based on: (1) leaching with sulphuric acid, or (2) leaching with alkaline carbonate solutions.

The choice of leaching method is dependent upon the mineral content of the ore. Alkali carbonate leaching is indicated when the acid consuming minerals are expected to exceed economic limits, and providing that the ore does not contain an excessive amount of minerals that consume sodium carbonate, such as iron sulphides.

The principal producing mines derive their ore from hydrothermal vein deposits.[3,4] Such deposits invariably contain carbonate minerals, principally calcite, but also siderite, rhodocrosite, etc., that are soluble in weakly acid solutions. It is, however, remarkable that the carbonate contents of the ores now being mined varies between rather narrow limits, and ores that contain sufficient acid soluble minerals to rule out acid leaching are very rare.

Besides carbonates, the vein type uranium ores contain appreciable amounts of chlorite minerals which consume a certain amount of acid. Hematite is also present in appreciable amounts but only the earthy type of hematite is soluble in the weakly acid solutions. Specular hematite predominates over the earthy type.

Sulphide minerals are commonly associated with pitchblende. Most sulphides are not soluble in the cold solutions; exceptions are for instance pyrrhotite, marcasite and bornite. Many sulphides are, however, soluble to a considerable degree in hot sodium carbonate solution and, if appreciable amounts of these minerals are present, they must be removed by flotation prior to carbonate leaching. Similarly, carbonate minerals can be separated by flotation prior to acid leaching.

The cobalt-arsenide minerals that are present in abundance in ores of the Port Radium type are partly soluble and introduce certain complications; apatite and fluorite are also attacked to some degree. Graphite is abundant, but unaffected by the solutions.

The physical and chemical characteristics of the pitchblende grains are quite variable and of major importance as regards treatment.

Since tetravalent uranium compounds are the most difficult to dissolve or to maintain in solution, the presence of UO_2 in pitchblende requires addition of oxidising agents for successful acid leaching, or the ore pulp must be aerated for a prolonged period when alkali carbonate leaching is used.

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Port Radium pitchblende contains on the average a much greater ratio of UO_2/UO_3 than the Beaverlodge type pitchblende. In the latter type of mineral UO_3 predominates.

Secondary minerals containing hydrated silicates, carbonates or vanadates of uranium are not of importance in Canadian production, except that the Gunnar Mine on Lake Athabasca contains considerable uranophane.

The secondary minerals are readily dissolved by weak acid or by carbonate solution without oxidising agents.

As previously mentioned, the association of pitchblende with other minerals is very intimate. Even after grinding to minus 200 mesh the individual grains will usually contain inclusions of sulphides, calcite or silicates. This intimate mixture does not normally affect the extraction of uranium by leaching but is detrimental to the success of processes for pre-concentration of uranium ores. Minute grains of pitchblende are occasionally enclosed in silicate minerals or in calcite, thus preventing contact with the leach liquor. Extremely fine grinding is necessary if a considerable part of the uranium occurs in this manner, but this is an infrequent occurrence.

The ore from hydrothermal veins will generally contain in abundance such minerals as chlorite, graphite, carbonates and clay. These minerals are readily slimed and careful grinding and avoidance of violent agitation of the ore pulp is advisable in order to minimize troubles with settling, filter capacity and soluble losses of uranium.

Essentially all the Canadian production of uranium originates from pitchblende, but the mineral "Brannerite" is a potentially important source since this mineral is the principal value in the important new Blind River area.

Brannerite, a titanate of uranium, contains uranium in the hexavalent form; in the Blind River deposits altered Brannerite occurs in the matrix of a quartz pebble conglomerate associated with a considerable amount of pyrite. Minor amounts of uranium oxides and thucolite are also present.

Uraninite and uranothorite are the important minerals in the Bancroft deposits in the Ontario province.

Both Blind River and Bancroft ores are suitable for acid leaching since they contain only minor amounts of carbonate minerals. The Bancroft ores are of pegmatitic type and contain the uranium minerals in well defined crystals.

LEACHING METHODS

Acid Leaching[2]

The flowsheet includes grinding in water to minus 48 mesh followed by thickening and filtration; filtration may be omitted or only part of the thickener underflow may be filtered, depending on the settling characteristics of the ore; the aim is to obtain a density of 55 to 60% solids in the feed to the leaching section.

Settling agents are generally required in order to maintain a clear overflow from the thickener. (An alternative method of preparing leach feed is to crush and grind in air-swept mills. This system has not been in operation in Canada so far, except on a pilot plant scale, but it offers attractive possibilities on account of the reduction in slime content with consequent improvement of filtering rates and reduction in soluble losses.)

The pulp is acidified by sulphuric acid and sodium chlorate is added as an oxidising agent. Agitation is performed in airlift rake type agitators. Tanks are of wood or of rubber-lined steel, and stainless steel or rubber-covered material is used for the agitator mechanism. The leaching takes place at or near room temperature for about twenty-four hours. The flow is continuous.

The leached ore goes to two stages of filtration, the filter cake being washed and re-pulped by very dilute solutions of sulphuric acid. A final water wash follows. The combined filtrate is sent to the precipitation section.

The recovery of uranium from solutions may be accomplished by precipitation as a uranous phosphate or arsenate under controlled conditions. Alternatively the solution may be subjected to ion exchange. A few ores yield solution of such purity that uranium may be precipitated by direct neutralization with magnesia. The barren solution is sent to waste or part of the solution is re-cycled.

The filtration of leach residues may offer certain difficulties when appreciable amounts of calcium sulphate are formed in the process. Flocculating agents must then be used in order to obtain reasonable filtration rates.

Successful leaching requires close control of solution composition, particularly when the ores yield soluble compounds that tend to precipitate uranium prematurely during agitation. It is also necessary to maintain close control of acidity, since excess acidity is wasteful, and to regulate closely the content of sodium chlorate. The latter compound has been found to be the most convenient oxidizing agent for Canadian plants.

Leaching in Alkali Carbonate Solutions[2,5,6,7]

The ore is ground in 5% carbonate solution, thickened and leached. The leaching takes place at elevated temperatures and aeration of the pulp is required for oxidizing the tetravalent uranium in pitchblende.

Leaching may take place in autoclaves or in Pachuca tanks at about 55% solids. In the former case the temperature of the pulp is 220–230°F, in the latter case about 160–170°F. The solutions must contain appreciable amounts of bicarbonates in order to obtain a satisfactory extraction. These bicarbonates are formed by reaction of the normal carbonate with sulphide minerals or may be formed by the addition of fluegas.

The leached ore pulp is cooled by heat exchange with the incoming leach feed and the solution is separated from residue by double filtration or by washing thickeners followed by filtration.

The pregnant solution is treated with sodium hydroxide to precipitate uranium as a sodium diuranate, and the barren solution is re-cycled after passing through a carbonation tower where excess caustic soda is converted to sodium carbonate.

The carbonate solutions are expensive and must be re-cycled.

Sulphide minerals are the principal consumers of carbonate and sodium sulphate is formed. The high content of chemicals influences filtering rates and flocculating agents are frequently required.

Choice of Process and Variations of Flowsheets

Simple acid leaching is generally indicated for ores containing pitchblende, uraninite, uranothorite, etc., providing that the content of carbonate minerals is not excessive. If the ore contains soluble carbonates corresponding to more than 4% CO_2, flotation of carbonates must be considered, followed by separate leaching of the flotation concentrate in alkaline solutions.

Alkali carbonate leaching is indicated for ores that contain a large amount of calcite. If, however, the sulphur content of the ore is higher than 0.4–0.5%, the sulphide minerals must be removed by flotation for separate treatment. The sulphide minerals are more or less completely decomposed by the hot alkaline solutions and are the principal consumers of reagents.

It has been found that leaching in alkaline carbonate solution requires a finer grind than that required for acid leaching. Also, the filtration of residues is rather more difficult when carbonate leaching is employed due to the heavy build-up of soluble salt in circulating solution.

On the other hand, the precipitation of uranium from carbonate solution is a simpler and cheaper process than precipitation from acid solution and the capital cost of acid proof filters and of an acid manufacturing plant is avoided.

The overall recoveries by acid leaching are generally a few per cent higher than by alkaline leaching.

ALTERNATIVE METHODS IN THE DEVELOPMENT STAGE

The methods employed or planned for treatment of Canadian ores were developed or modified in Canada, except the precipitation through ion exchange which will be incorporated in several new treatment plants.

Certain other leaching methods have been developed on a laboratory or pilot plant scale.

Thus, many ores will respond to leaching by SO_2 solutions followed by aeration and the uranium may be readily precipitated from the resulting solutions by iron powder plus a soluble phosphate.

Uranium has also been extracted by leaching sulphidic ores in autoclaves at relatively high temperatures and pressures. Aeration of the pulp produces sufficient acid through oxidation of sulphides to extract uranium.

The first Canadian method for carbonate leaching of uranium from original pitchblende ores was developed in 1950–51. This method was characterised by the use of soluble permanganates (instead of aeration), and precipitation of uranium by sodium hydroxide. Two to ten pounds of permanganate was the usual consumption. The "permanganate leach" was the basis from which the chemistry and practice of the present Beaverlodge treatment methods were developed.

Alternative methods for precipitation of uranium from carbonate solution as UO_2 have been pilot plant tested.

METHODS OF PRE-CONCENTRATION

Uranium leaching is expensive, as regards both capital and operating costs, and test work has been carried out with many ores in an attempt to reduce the leach plant feed by pre-concentration.

Methods available that may apply to some Canadian ores are: "heavy media separation," "flotation," "electronic sorting" and "gravity concentration."

Heavy Media Separation

The uranium minerals are often associated with hematite, sulphides or other heavy minerals in such a manner that the ore may be concentrated by heavy media separation. Occasionally, the conventional type of sink-and-float at coarse size, say 1½ in. to ⅛ in., will yield satisfactory rejects as regards quantity and uranium content. For other ores a fine crush to say ¼ in. is required in order to free the uranium-heavy mineral aggregates; the cyclone type of heavy media separation is often indicated for such ores. This latter method gives effective separation of ore as fine as forty-eight mesh, using a magnetite medium. To date, the test work on such methods has not been carried beyond the pilot plant but the results are of definite interests for certain deposits.

Flotation

Flotation of pitchblende is not employed on a commercial scale in Canada. However, extensive test work has indicated that flotation will be of economic benefit for certain ores, particularly for ores of the pegmatite type that contain well defined crystals of uraninite, uranothorite or columbate-tantalate minerals of uranium; many of these ores contain gangue minerals that are rather easily depressed and recoveries of 90% with a 5:1 ratio of concentration have been obtained.

For ores from hydrothermal veins the pre-concentration by flotation is somewhat more difficult because much of the pitchblende is so intimately mixed with chlorite, hematite and calcite that release by grinding is not feasible.

Flotation of the latter type ore is based on depression of barren gangue minerals such as quartz and feldspar, while hematite, chlorite, graphite, etc., report in the concentrate. Recoveries of 85% with a 1 : 3 ratio of concentration have occasionally been obtained.

Electronic Sorting

The Lapointe Picking Belt is applicable to treatment of coarse ore in the size range 8 in. to 1½ in. Rejection of waste will range from 30–40% of the ore tonnage mined.

Gravity Concentration

Pre-concentration by jigs, tables, etc., is suitable for certain pegmatite ores.

The future progress towards reduction of capital and operating costs for uranium treatment plants will depend to a large extent on efficient methods of pre-concentration.

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Method for Chemical Processing of Low-Grade Uranium Ores

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The chemical procedures generally employed for treating uranium-bearing ores consist of an acid digestion followed by separation of the insoluble residue, treatment of the resultant solution with an excess of sodium carbonate, which precipitates the foreign elements and leaves the uranium in solution in the form of a complex: sodium uranyl carbonate. After precipitated hydroxides are filtered out, the sodium uranyl carbonate is decomposed either by neutralization with an acid or by addition of caustic soda, and converted into sodium uranate.

In order to accumulate quickly the amounts of uranium needed for the construction of its first piles, the CEA concentrated its efforts on the production of of uranium from the richest ores it had available.

To this end a chemical treatment plant was constructed, using a process akin to the one described above.

Because of constantly increasing uranium requirements and the fact that this element is mainly found in low-grade ores, it became necessary to treat the latter class of ore.

Economic factors precluded employment of the standard processes. Their uranium extraction efficiency is low, depending as it does on the richness of the ore, and their cost is high.

Since treating low-grade uranium ores would make it possible to increase the available tonnage of uranium considerably, we looked for processes that would enable us to obtain this element at a reasonable cost.

We envisaged sulfuric acid digestion because of price, ease of storage, the possibility of using less costly materials, and also in order to make it possible to use processes based on reduction.

As for the treatment of the digestion solutions, it was found that when the ore is rich enough, uranium is separated from its principal impurities by precipitating the latter from solution; when dealing with low-grade ores, the ratio of the fraction of dissolved impurities to the fraction of uranium in solution becomes very high. The idea of effecting separation of the uranium impurities by precipitating the small fraction, namely the uranium, by means of one or more suitable reagents was attractive. The quantities of these reagents would be functions of the element in question, and whose properties would be such as to leave the digesting solution virtually unaltered.

In this way we avoid the separation of large precipitates. Application of such a process would also make possible more complete recovery of the uranium. On the other hand, if the impurities were precipitated beforehand, there would be a risk of considerable loss by adsorption since the amount of uranium is small compared to the amount of the impurities.

We investigated in what form the uranium could be extracted. The problem was to precipitate the uranium in an acid medium in such a way as to leave the foreign metals in solution. The principal salts of uranium that are insoluble in an acid solution are those with a valence of four. Among these we selected uranous phosphate and insoluble uranous pyrophosphate, obtaining them by precipitation in an acid medium after reducing the dissolved uranium(VI) to uranium(IV). There are thus two distinct phases in the contemplated process: (1) reduction of the uranium within the solution from valence(VI) to valence(IV); (2) addition of a phosphate or soluble pyrophosphate forming an insoluble salt of tetravalent uranium.

We used the insolubility of the phosphates because the ores often contain phosphates, so depending on their content of that substance the uranium could be precipitated with less or no added phosphate ion.

LABORATORY EXPERIMENTS

First Variant: Uranous Phosphate

The laboratory tests were concerned primarily with a choice among the various reducing agents suitable for industrial use, namely: (*a*) sodium hydrosulfite, (*b*) metallic aluminum, and (*c*) iron turnings (metallic chips obtained by milling).

Sodium Hydrosulfite

Reduction can be effected by sodium hydrosulfite, a reducing agent that has given us excellent results.

In order to perfect the process, we made experiments on sulfuric acid solutions of low-grade uranium ores, in which the following factors were studied: (*a*) determination of the amount of sodium hydrosulfite required (Table I); (*b*) influence of the amount of P_2O_5 employed (Table II); (*c*) influence of the final acidity (Table III); (*d*) influence of the

Original language: French.

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Table I. Determination of the Amount of Sodium Hydrosulfite*

Amount of hydrosulfite in grams/gram U	*U content of filtrate after precipitation, mg/liter*	*Precipitation efficiency*
0.2	860	14.0
0.6	550	45.0
1.0	190	81.0
1.1	97	95.3
1.2	45	90.5
1.4	22	97.8
1.5	19	98.1
2.0	17	98.3
3.0	14	98.6
6.0	11	98.9

* The digestion solution contained: uranium, 1 gm/liter; acidity, pH2; P_2O_5, gm/liter. Temperature was 60°; stirring time was 30 min.

temperature (Table IV); (*e*) influence of the uranium content of model solutions treated (Table V).

According to Table I, the amount of sodium hydrosulfite should be in the ratio: hydrosulfite/uranium = 3.

The test described by Table II shows that there is no point in going beyond 3 gm of P_2O_5 per gram of uranium.

The test in Table III shows that in order to get a high yield the final acidity must be brought to pH 2, since the uranous phosphate is soluble at higher acidities.

As shown in Table IV, the solubility of uranous phosphate is not notably changed when the temperature is raised.

The study in Table V indicates that about 3 kilograms of sodium hyposulfite must be used per kilogram of uranium for the given ores; that the amount of PO_4^{---} ions present in the solution should equal at least 3 kg, calculated as P_2O_5 per kg of uranium; that the final pH should be about 3; that the temperature does not have any very marked effect; and that the precipitation efficiency increases with the uranium concentration of the initial solution.

It is understood, of course, that the amounts of sodium hydrosulfite and of phosphate necessary for precipitation are not functions exclusively of the U content of the solutions, but also depend on the foreign elements that can react with these products.

When the solutions initially contain an insufficient amount of phosphate ions it is advisable to adjust the content by adding sodium phosphate and to do this before reducing, since the uranium precipitates during the reduction.

If the residual acidity of the digesting liquors is too great, the pH of the solution must be adjusted before reduction, so as to obtain a good precipitation yield.

We may note that for one of our ores, for which the content of the digestion solutions varied from 0.8 gm to 2 gm of uranium per liter, we obtained residual liquors containing between 7 and 15 mg of uranium per liter after precipitation of the uranium, and precipitates containing the uranous phosphate with dry assay values of 15 to 20% of uranium.

Table II. Influence of the Amount of P_2O_5 Applied*

Amount of P_2O_5 in gm/liter	*U content of filtrate after precipitation, mg/liter*	*Precipitation efficiency, %*
0.25	505	49.5
0.375	340	66.0
0.562	335	66.5
0.75	170	83.0
1.5	28	97.2
3.0	17	98.3
6 0	15	98.5

* The digestion solution contained: uranium, 1 gm/liter; sodium hydrosulfite, 3 gm/liter. Acidity was pH 2; temperature, 60°; stirring time, 30 min.

Table III. Influence of the Final Acidity*

Acidity	*U content of filtrate after precipitation, mg/liter*	*Precipitation efficiency, %*
2 *N*	960	4.0
1 *N*	710	29.0
0.5 *N*	93	90.7
0.1 *N*	31	96.9
pH 2.05	18	98.0

* The digestion solution contained: uranium, 1 gm/liter; P_2O_5, 3 gm/liter; sodium hydrosulfite, 3 gm/liter. Temperature was 60°; stirring time, 30 min.

Table IV. Influence of Temperature*

Temperature	*U content of filtrate after precipitation, mg/liter*	*Precipitation efficiency, %*
20°	24	97.6
30°	17	98.3

* The digestion solution contained: uranium, 1 gm/liter; P_2O_5, 3 gm/liter; sodium hydrosulfite, 3 gm/liter. Acidity was pH 2; stirring time, 30 min.

This study indicates that sodium hyposulfite is a suitable reducing agent for quantitatively precipitating uranium in a medium containing phosphate ions, but its price is relatively high. An attempt was made to find whether it could be replaced by less expensive reducing agents, such as aluminum or iron.

Metallic Aluminum

With solutions produced by digestion of ore, experiments on reduction with aluminum gave precipitation yields of 86%. However, reduction tests in the presence of sodium sulfite or sodium hydrosulfite gave precipitation yields of 98.9%. The P_2O_5/U ratio is 3, as in the case of a sodium hydrosulfite reduction.

Although the results obtained were encouraging, we turned toward the use of iron, which is cheaper.

Iron

Reduction by means of iron was likewise studied on sulfuric acid solutions of low-grade ores.

The following points were examined:

Influence of the amount of P_2O_5 *applied*: The tests made have shown that the quantity of P_2O_5 necessary for the total precipitation of uranium must be equal to 3 gm/gm of uranium.

Table V. Influence of the U Concentration*

Concentration, U gm/liter	*U content of filtrate after precipitation, mg/liter*	*Precipitation efficiency, %*
3.0	6	99.4
1.0	17	98.3
0.5	18	96.4

* The solution contained: P_2O_5/U ratio, in grams, = 3; hydrosulfite/U ratio, in grams = 3; acidity = pH 2; stirring time = 30 min.

Influence of the amount of iron applied: The experiments were conducted in the cold by adding disodium phosphate after the reduction had been completed and the solution separated from the excess iron, with a digestion solution containing 1.58 gm of uranium per liter and with an initial acidity of 0.75*N*.

The results are given in Table VI.

These results indicate that the reduction is the more rapid the greater the amount of iron applied, that is, the flow of nascent hydrogen is greater. The amount of iron consumed obviously depends only on the initial and final acidities. The consumption of iron in these experiments is about 10 parts for one part of uranium.

Influence of temperature: With the same initial solution, at a temperature of 50°, with 21 parts of iron and 3 parts of P_2O_5, applied per part of U, we obtained in 1½ hour: final acidity, 0.23*N*; acid consumed 0.52*N*; iron consumed, 9.2 gm/gm U; U in the filtrate, 61.0 mg/liter; and precipitation efficiency 96%.

The reduction is faster at 50° than at room temperature, other things being equal; on the other hand, increasing the temperature has no appreciable effect on the precipitation efficiency.

Influence of the final acidity on the precipitation efficiency: The experiments were made under the following conditions: U content of initial solution, 0.875 gm/liter; initial acidity of solution, 0.7*N*; amount of iron applied, 60.0 gm/gm U; amount of P_2O_5 applied (as disodium phosphate), 3.0 gm/gm U; temperature, 50°. The acidity and the U content of the solutions were measured on samples taken at regular intervals. The results are given in Table VII. The results indicate that to obtain an acceptable precipitation efficiency it is sufficient to end the reduction at a pH lying between 2 and 3.

Comparison of Sodium Hydrosulfite and Iron Procedures

The researches conducted with sodium hydrosulfite and iron show that in both cases: The P_2O_5/U ratio should be equal to 3. The reduction should be ended with a pH lying between 2 and 3. The temperature has no appreciable effect on the precipitation efficiency.

Table VII

Final acidity N	*U content of filtrate after precipitation, mg/liter*	*Precipitation efficiency, %*
0.60	580	34
0.52	335	62
0.46	150	83
0.33	80	91
0.20	55	93.5
0.07	35	96
pH 3	10	98.8

Since the results are satisfactory with both contemplated procedures, comparison of the consumption and prices of the two reagents led us to adopt the iron process for industrial use.

Second Variant: Uranous Pyrophosphate

The precipitation of uranium from the sulfuric acid solutions resulting from digestion of the ores can be improved, under the process previously described, by a variant which consists in isolating the uranium(IV) in the form of the pyrophosphate.

The advantage of this salt is its low solubility which is less than that of uranous phosphate, thus making it possible to work at higher acid concentrations.

The result is that the proportion of impurities precipitating with the uranium decreases and subsequent operations deal with a richer and purer product and may be confined to a soda treatment without preliminary carbonate formation.

The optimum conditions for precipitation of uranium pyrophosphate depend on various factors: (*a*) hydrogen ion concentration; (*b*) relative sodium pyrophosphate concentration; and (*c*) foreign ions present in the solution.

The effect of these factors was studied in solutions of uranyl sulfate and synthetic mixtures, which were reduced by zinc amalgam in order to get the uranium(VI) into valence (IV).

Influence of the Hydrogen Ion Concentration in the Solution

250 ml of a solution of uranyl sulfate containing 250 mg of uranium were treated, after reduction, with sodium pyrophosphate. The uranium remaining in the filtrate was determined by the fluorimetric method. The results are given in Table VIII. It will be seen that the solubility of uranous pyrophosphate remains very low up to 1*N* acidity. It then increases,

Table VI

Stirring time, hours	*Acidity*		*gm iron/gm U*		*P_2O_5 introduced gm/gm U*	*U content of filtrate after precipitation mg/liter*	*Precipitation efficiency, %*
	Final N	*Consumed N*	*Applied*	*Consumed*			
½	0.65	0.10	32	1.77	3	385	75
2½	0.35	0.40	21	7.1	3	78	95
1½	0.20	0.55	52	9.7	3	50	97
½	0.20	0.55	105	9.7	3	48	97

Table VIII

Acidity of solution, N	*U content of filtrate after precipitation mg/liter*
0.25	7
0.5	6
1.0	8
2	25
3	36
4	150
6	1000

and becomes complete at acidity 6*N*. It should be noted that the solubility of uranous pyrophosphate is independent of the uranium concentration of the solutions.

Influence of the Relative Concentration of Pyrophosphate Ions in the Solution

Uranium pyrophosphate dissolves in an excess of sodium pyrophosphate. This led us to study the limiting values for the use of this reagent. As the results in Table IX indicate, this is between 1.25 and 2, referred to the $Na_4P_2O_7/U$ ratio. It is therefore broad enough to obviate the need of operating with a rigorously exact amount of sodium pyrophosphate.

Table IX

$Na_4P_2O_7/U$	*U content of filter after precipitation, mg/liter*
1.25	7
2	8
3	20
4	45

Influence of Foreign Ions

The foreign ions present in solution along with the uranium may interfere with the precipitation of uranium pyrophosphate: (*a*) by reacting with the sodium pyrophosphate; (*b*) by forming complexes with the uranium; or (*c*) by acting as catalyst for oxidations, like Fe^{+++}, or as a flocculation inhibitor.

Above all we investigated the influence of iron which, together with aluminum, is the principal impurity of the solutions produced by digesting our ores. These solutions likewise contain phosphates and a little fluorine which can completely prevent the precipitation of the uranium when it does not form a complex.

The ferric iron is precipitated by the sodium pyrophosphate. On the other hand, aluminum and ferrous iron do not precipitate at the acidities at which we operate (0.5*N* and 1*N*). Consequently, sodium pyrophosphate must be added to the previously reduced solution.

Table X

Content of solutions, mg/liter	*U content of filtrate mg/liter without oxidation*	*Precipitation efficiency, %*	*U content of filtrate mg/liter with oxidation until phenosafranine changes color*	*Precipitation efficiency, %*
1000	71	93.0	12.2	98.8
1000	93	91.0	20.0	98.0
1000	130	87.0	17.0	98.3
1000	75	92.5	9.8	99.2
1000	72	92.8	10.0	99.0
1000	43	95.7	11.0	98.9

When the uranium solutions contain iron, the solubility of uranium pyrophosphate increases.

The amount of uranium found in the filtrate after precipitation rises from 7 ppm to 25 ppm. This is due to the rapid oxidation of the Fe^{++} upon contact with the air, and of the U(IV) by Fe^{+++}. This obstacle is eliminated by adding thiosulfate.

After studying the principal factors that can affect the precipitation of uranium pyrophosphate, we endeavored to adopt the results obtained to an industrial process, fixing the experimental conditions as follows:

(*a*) The sodium pyrophosphate should be added after the reduction of the solution.

(*b*) The acidity of the medium should not be above 1*N* at the moment of precipitation.

(*c*) The amount of sodium pyrophosphate required lies between values 1.15 and 2 of the molecular ratio $Na_4P_2O_7/U$. (In our experiments on the digestion solutions, we use a ratio of 2.)

When iron is used to reduce the sulfuric acid digestion solutions, at a temperature of 50°, sulfides are formed which affect the solubility of uranium pyrophosphate. It is essential to reoxidize the solutions with air after adding the sodium pyrophosphate, checking the oxidation-reduction potential with phenosafranine, in order to obtain better precipitation efficiency of the uranium pyrophosphate.

In the solutions investigated (Table X), having a free acidity of 0.8*N*, the reduction is completed at pH 0.7. At this pH we observed only a very slight precipitation of uranous phosphate (less than 2 mg U/liter), due to the phosphate ions present in solution.

The last result enables us to filter the digestion after the reduction and before the precipitation of the uranium, in order to eliminate the insoluble sulfides formed during the reduction of the particles of metallic iron remaining in suspension.

The pyrophosphates obtained assay 25 to 30% of uranium.

The principal impurities they contain are iron as ferric pyrophosphate (which is formed upon reoxidation of the sulfides by the oxygen of the air), a little aluminum, and some silica.

Subsequent treatment of the uranium pyrophosphate with sodium hydroxide, the purpose of which is to eliminate certain impurities (phosphate, alumina, silica), makes it possible to obtain products assaying between 50 and 60% of uranium.

There are two advantages of isolating the uranium in the form of uranous pyrophosphate: the first is that it enables us to obtain a precipitate that is richer in uranium (25 to 30%), in a more acid medium, and thus to increase the capacity at the filter presses.

The second advantage is elimination of the carbonate step which is required in the case of uranous

phosphate, by direct soda treatment of the precipitate. This enables us to make substantial savings.

DESCRIPTION OF THE INDUSTRIAL APPLICATION

The process of precipitation of uranous phosphate after reduction with iron has been adopted in the first French factory treating low-grade ores chemically, and has proved to be perfectly practicable.

This factory is located at Gueugnon (Saône-et-Loire) and processes ores from the deposits at Grury. It was constructed in 1954 for the CEA by the Société Potasse et Engrais Chimiques, which likewise perfected the process, which comprises: (*a*) crushing the ore, which contains about 1% of uranium; sulfuric acid digestion hot; and separation of the digestion solution from the gangue by continuous filtration; (*b*) reduction-precipitation of the uranium by adding iron turnings and phosphates followed by filtration of the precipitate; (*c*) conversion of the uranous phosphate contained in the precipitate into sodium uranate.

Crushing the Ore

The low-grade ores we treat, composed in large part of quartz and silica (60 to 80%), contain only a small portion of soluble elements (5 to 10%), among which is included uranium, in various mineralogical forms: pitchblende, autunite, chalcolite, gummite, etc. The uranium content of these ores varies between 0.6 and 1.2%.

Crushing of the mineral is performed in three stages: primary crushing in a jaw crusher, reducing the size from 300 to 60 mm; secondary crushing in a gyratory crusher, reducing the size from 60 to 25 mm; and tertiary wet grinding in a rod mill, reducing the ore to 40 mesh.

After sizing, the sludge obtained is sent to a thickener, which supplies the digesting tanks via a diaphragm pump.

The sulfuric acid digestion is performed by concurrent flow at a temperature of 70° in four rubber-lined tanks, with a solid/liquid ratio of 0.75, and the amount of sulfuric acid equal to 150 kg per ton of ore, in order to obtain solutions with the greatest possible uranium concentration.

In order to cut down the consumption of sulfuric acid, we digested the ore in the presence of manganese dioxide; whenever the ore contained uranium in the form of pitchblende we were able to reduce the consumption by two-thirds in this way.

The gangues produced by digestion are filtered on a rotating continuous horizontal filter (constructed by the Engineering and Industrial Corporation, Luxembourg) and washed with hot water. The digestion solutions and the wash water, totaling a volume of 1600 liters per ton of ore treated, are then sent to the reduction stage.

Reduction-Precipitation of Uranium

The filtered solution contains 0.6–1 gm per liter of uranium with valence (VI), 0.75*N* of free sulfuric acid, and in general enough P_2O_5 to precipitate the uranium, the P_2O_5/U ratio being equal to 3. If the quantity of P_2O_5 is insufficient, additional phosphate is added.

The solution is raised to a temperature of 500° to increase the reduction rate. (The temperature only slightly affects the solubility of uranous phosphate.)

Reduction is then effected by adding more iron turnings than is necessary to bring the acidity to a pH between 2 and 3. We have always observed that starting with an acidity of 0.75*N*, the amount of iron was enough to reduce not only the uranium, but also the iron resulting from the digestion, as well as the other reducible elements.

The uranous phosphate precipitates out as the reduction and neutralization go forward.

The operation takes about an hour. Decantation is performed in such a way as to eliminate a maximum of suspended iron, and the phosphate is filtered on a filter press.

The cake obtained contains iron sulfate, originating both in the ore digestion and in digestion of the iron turnings used in the reduction. It is washed with water so as to eliminate most of the iron sulfate.

Upon being taken from the mold, the cake contains 50% moisture and about 10% of uranium, calculated on the basis of the dry substance. The principal impurity is metallic iron that has been swept along.

Conversion into Sodium Uranate

The cake containing the uranous phosphate is taken out and put into suspension in the proportion of 1 ton of wet cake to 3200 liters of water. One ton of anhydrous sodium carbonate per ton of wet cake is then introduced. After dissolving the sodium carbonate, 100 kg of sodium permanganate dissolved in a minimum quantity of water is added. The temperature is raised to 90°, and it is stirred for 8 hours at that temperature.

The product is then filtered on a filter press; the cake containing the impurities is washed with hot water, about 2500 liters per ton of cake. The residue is then eliminated.

The uranium present in the solution in the form of sodium uranyl carbonate is then precipitated out by adding soda; and filtration yields a cake of sodium uranate whose uranium content, on a dry basis, is about 65%; this is then sent to our central factory at Bouchet (Seine-et-Oise) for refining and conversion into the metal.

CONCLUSION

The procedure shows that it is possible to extract uranium chemically from ores of this sort containing 1% of uranium and even to go down to contents of the order of 0.5% and even less, and obtain an end-product in the form of sodium uranate containing 60–65% uranium, with a reasonable cost price and a total extraction efficiency of between 90 and 95%.

Recovery of Uranium from Uranium Bearing Alum Shale

By Erik Svenke,* Sweden

So far uranium bearing alum shale represents the only known deposits of uranium ore in Sweden which are extensive enough to make them important as source material for an industrial recovery of uranium. The recoverable amount of uranium in shale averaging about 200 grams of U/ton is estimated to exceed 100,000 tons. The deposits are thus low grade but available in very large quantities.

As uranium is the only primary atomic fuel, a uranium industry based on domestic source material must be considered to be of vital interest to the country's future atomic energy program, and therefore, within the Swedish program, owing to the above-mentioned circumstances, considerable effort has been spent and is now being spent on developing industrial treatment methods for the recovery of uranium from these ores.

In some horizons of the richest shale layers there are to be found lenses of a highly carboniferous material, named "kolm," averaging about 0.3% uranium, i.e., substantially higher than the surrounding shale. In view of anticipated difficulties in developing treatment methods for the recovery of uranium from shale, and also because of the need to establish a small production very quickly, the first effort was started at the end of the 1940's with "kolm."

The specific gravity of "kolm" is lower than that of shale and it can therefore be separated by means of a so-called heavy-media technique, well known from ore-dressing technique, especially coal cleaning. For this purpose a small plant was built. It operated for some years, and the "kolm" produced was treated in a leaching process for uranium recovery.

It was, however, quite evident that the need of uranium for a future program could not be met in this way, and investigations were simultaneously carried out in order to obtain methods to recover uranium from the large quantities of the easily available shale, and the experience obtained from the "kolm" treatment was then of great help.

During the development period and up till the building of an industrial plant for the shale treatment, no information from abroad was available on this subject.

After the testing of the methods in a pilot-plant, a small industrial plant was constructed. It was put into operation in the summer of 1953 and has been running ever since. The factory scale requires an increase on the laboratory scale of 10,000 times. With such an increase in scale many problems will of course, occur, which have not appeared during the laboratory tests, i.e, problems of heat transfer and material handling. It must also be pointed out that the choice of the most suitable unit operations for carrying out unit processes worked out on laboratory scale is of great importance to the economic result.

These alum shales are sedimentary rocks formed through sedimentation of a sapropel in a shallow bay. Then it has been drained and subjected to metamorphosis. These shales are composed of silicates, mainly quartz and mica, microcrystalline pyrite and an organic kerogen substance. A typical chemical analysis is given in Table I.

The process used at the plant at present means a chemical leaching with sulphuric acid solution in several steps at about 60°C, the maximum concentration of the acid in the leaching being about 180 grams H_2SO_4/litre. The main part of the uranium content is then dissolved out at a much higher selectivity than the other inorganic components. Besides the uranium, many other ions, especially iron, aluminium, magnesium, potassium and titanium are, however, obtained in the solution.

The choice of the acid concentration of the leach solutions as well as the choice of the temperature at the leaching is a technical and economic matter. Higher acid concentration and higher temperature will result in the dissolution of more aluminium due to the decomposing of the more acid-resistant minerals, while lower concentration and lower temperature give a slower dissolution of the uranium. With the process in question the acid consumption should be kept at 65 kg H_2SO_4/metric ton of shale.

After the separation of the pregnant leach solution from the solid residue, the uranium is recovered by selective precipitation as a fourvalent phosphate, the necessary phosphate ions already being available in the solution due to the decomposing of the phosphates contained in the shale material. The precipitation has a remarkable pH-sensitivity, which can be seen from Fig. 1.

In addition, the character of the precipitation and its completeness also depend on the concentration of many of the other ions, and the most suitable conditions will thus vary for different kinds of solutions. This simple recovery process is therefore best applied to homogeneous basic materials, as in this case. The pregnant solution shows no large variation in its composition. After the precipitation process in such

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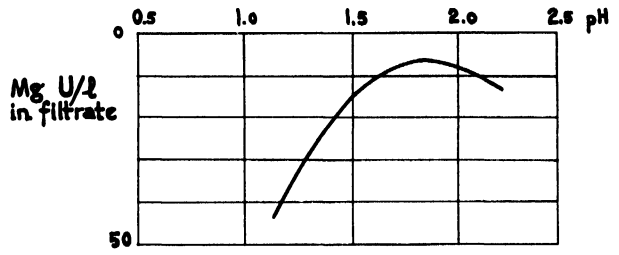

Figure 1. Mg U/l in filtrate

solutions a uranium content of about 10 mg/litre can be reached in the residue solution.

Other recovery methods can also be used for this kind of solution. In pilot scale units tests have thus been made with adsorption on anion exchange resins of the sulphate complex, in which the uranium is involved in these solutions, as well as with elution by means of sulphuric acid or chloride solutions. (In the laboratory model liquid extraction by means of alkyl phosphates has also been tested.)

In order to avoid stream pollution the solutions remaining after the recovery of uranium are treated with lime for neutralization and precipitation of iron and aluminium mainly. The resulting slurry is pumped to the dump for the solid leach residue where the precipitate is retained. The clear remaining solution is pumped into a small stream.

Of the various hydrometallurgical treatment methods available for the recovery of uranium from ores and similar products, the following possibilities can be considered: leaching of finely ground material under agitation and separation through filtration or sedimentation or percolation leach in sumps with filter bottom.

For technical and economic reasons percolation leach has been chosen, the choice being governed by many factors, for example the slimy character of finely ground shale which causes unfavourable filtration and sedimentation characteristics. Besides, leaching of a finely ground material gives only a small gain in yield as compared with the treatment of a somewhat coarser material. Waste disposal in the rather populous farming district where the plant is situated would also be very troublesome in case the residue should come out in form of a thickened underflow slurry instead of the easily self-draining residues after a percolation leach.

The percolation leach requires, however, a definite screen analysis of the feed material to permit a good dissolution within a reasonable time (i.e., the material should not be too coarse) as well as permitting satisfactory solution flow characteristics (i.e., not too finely ground material, containing no substantial quantity of dust). Thus the grinding system of the mill is of the greatest importance.

The actual ore body contains big lenticular concretions of bituminous limestone, causing a content of limestone in the run out of mine material. In order to lower the acid consumption in the leaching process a heavy-media separation unit is also included in the general flow-sheet treating the coarse crushed shale-limestone mixture in order to eliminate the limestone.

The flow-sheet for the plant is shown on Figs. 2 and 3.

Some details of the unit operations may be of general interest.

The heavy-media unit works with a feed −100 mm +6 mm and separates shale as a float product with a specific gravity of mainly 2.2 but partly reaching 2.5, and limestone as a sink product with a gravity of 2.6. As a medium a suspension of magnetite in water is used, the pulp containing around 32% solid iron oxide by volume. Magnetite in wash waters from washing screens for float and sink materials is recovered in the usual way by means of magnetic separators and before re-use demagnetized in a solenoid coil, as shown in the flow-sheet.

The prepared shale is fed to the vats by a stainless steel belt and a screw-conveyor movable over the vats and distributing the material evenly over the surface. A small quantity of steam is also fed into the conveyor causing a temperature rise in the feed and also an agglomeration of the dust to the coarser grains. These arrangements serve to avoid any sizing of the material, when fed to the vats as otherwise channelling may occur during the leaching causing uneven percolation.

The emptying of the vats is carried out by means of a special hydraulic device, developed for this purpose. Around the end of a rubber hose lowered in

Table I. Chemical Analysis. Moisture at a Temperature of 110°C = 0.74%

Loss on ignition: 650°C 26.06%	750°C 26.64%	850°C 26.95%	900°C 27.02%	970°C 27.36%
SiO_2 = 48.03%	U_3O_8 = 0.026%			
TiO_2 = 0.74%	Fe_2O_3 = 8.38 %	(S = 5.72% in dried sample)		
Al_2O_3 = 9.80%	MoO_3 = 0.05 %			
CaO = 0.56%	P_2O_5 = 0.17 %	SO_3 = 0.44% in sample calcined at 900°C		
MgO = 1.06%	MnO = 0.015%			
Na_2O = 0.30%	V_2O_5 = 0.008%	Loss on ignition = 27.02% in sample calcined at 900°C		
K_2O = 2.92%	Cr_2O_3 = 0.001%			
	CuO = 0.003%			
Total 63.41%	+ 8.65%	+	27.46% = 99.52%	

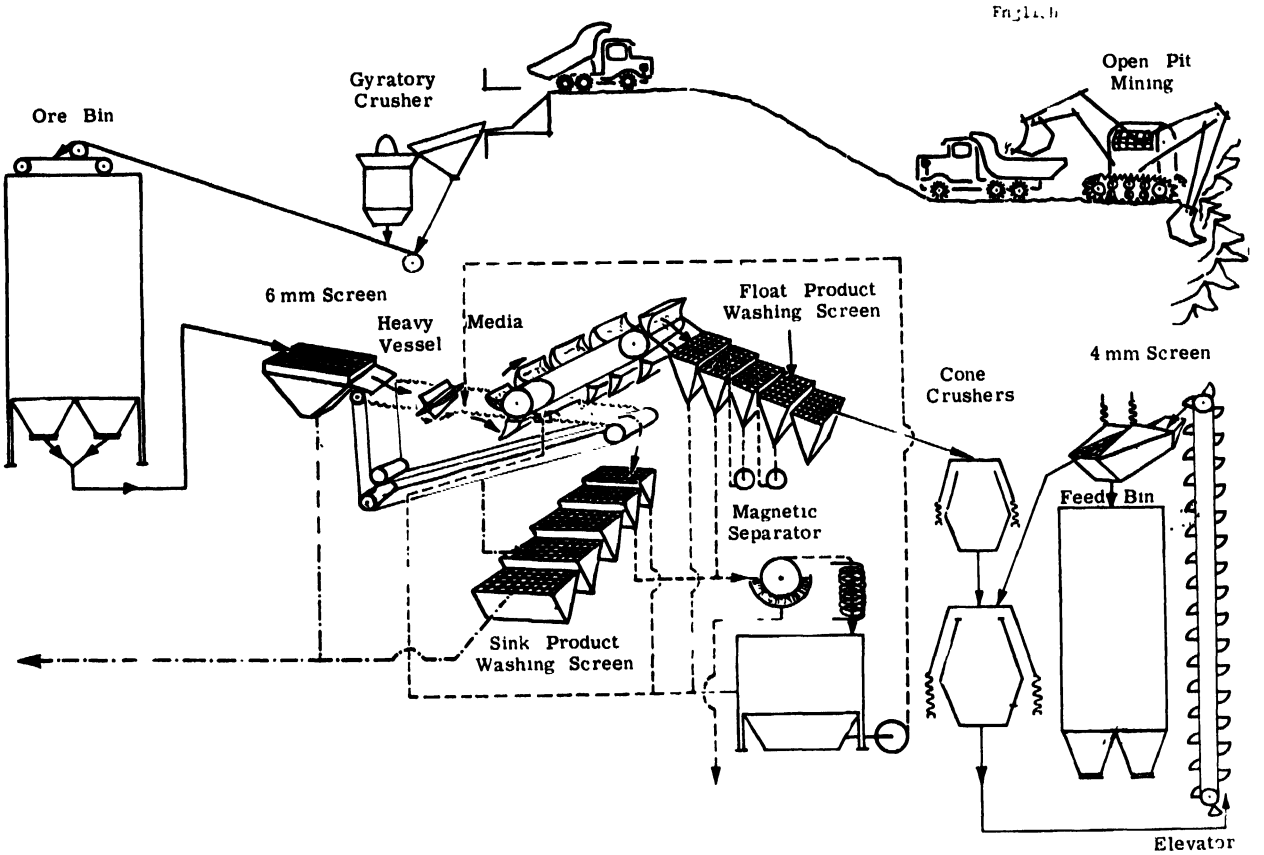

Figure 2

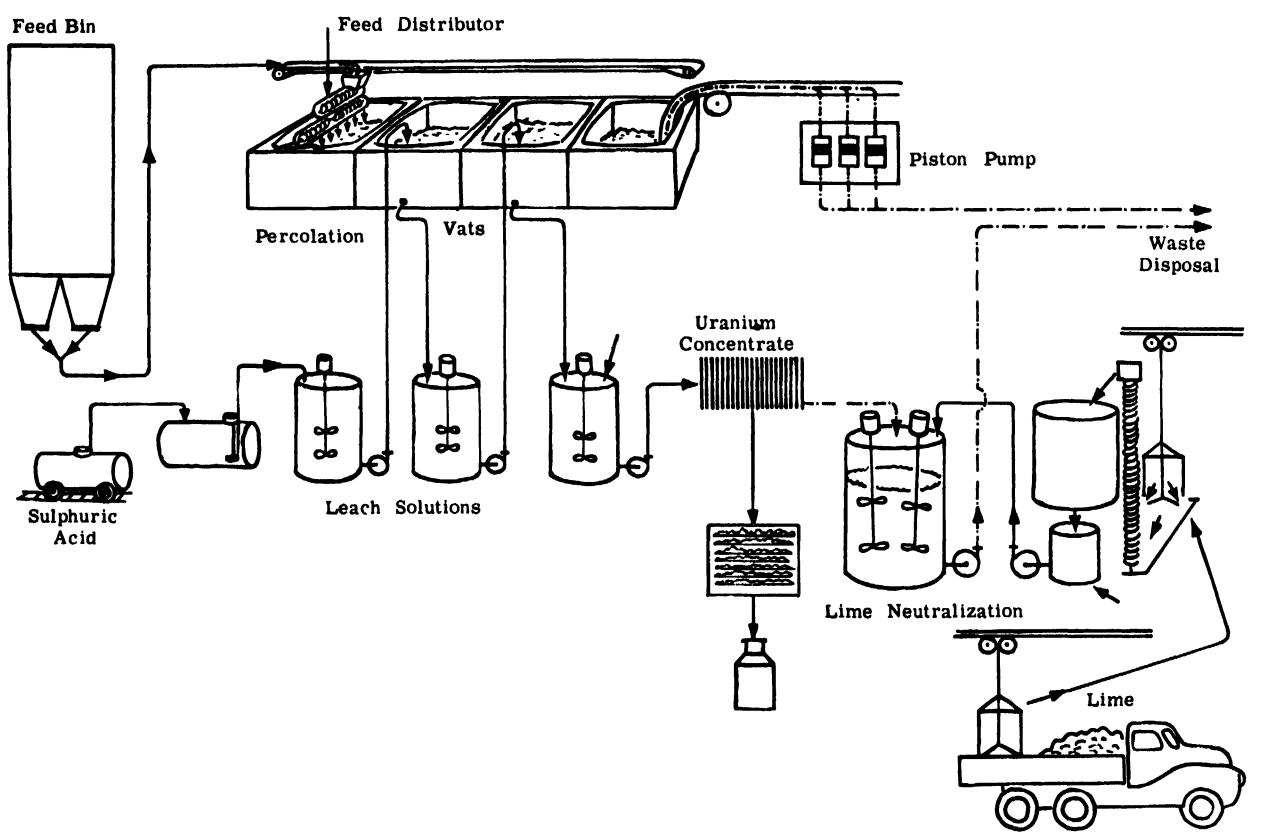

Figure 3

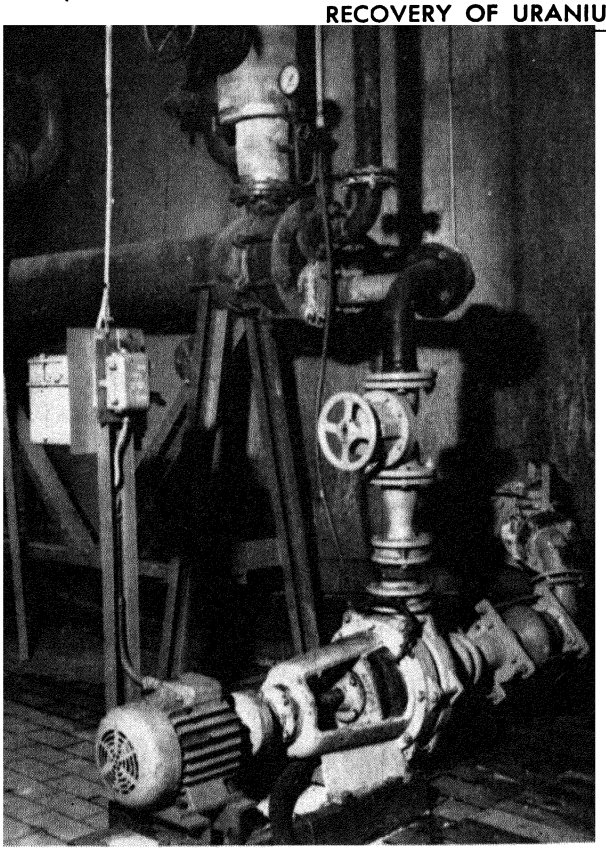

Figure 4. Karbate heat exchanger

the vat is formed a suspension from residue material and water. The rubber hose is connected to the suction side of a piston pump, and the suspension is suctioned out of the vat and pressed in one step through a pipeline to the dump, 400 meters from the plant.

As most of the solutions in the plant are strongly corrosive on metal constructional materials a range of acid resistant material had to be chosen to fit different needs in the operations. Thus, the following materials have mainly been used: acid-proof stone, rubber lining, plastic lining, rubber and plastic tubes and impervious graphite.

A couple of pictures (Figs. 4–6) will illustrate the operations.

An estimate of the industrial need of uranium in Sweden within 10 to 20 years presumes a yearly treatment of between 1 million and 2 million tons of shale, if all the uranium supply has to be recovered from this source material, i.e., a large but quite reasonable industrial operation.

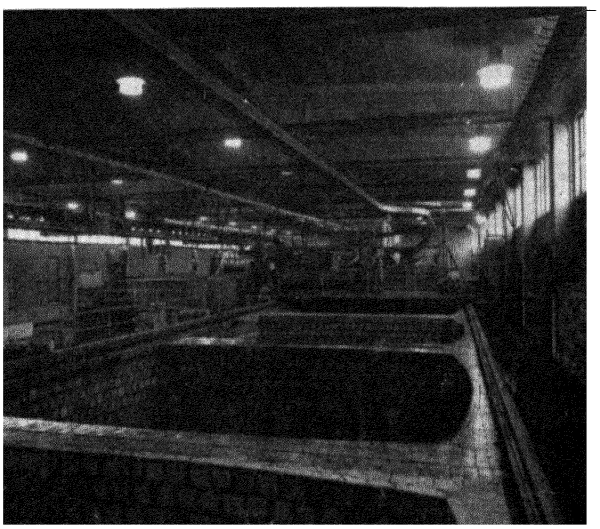

Figure 5. Percolation vats

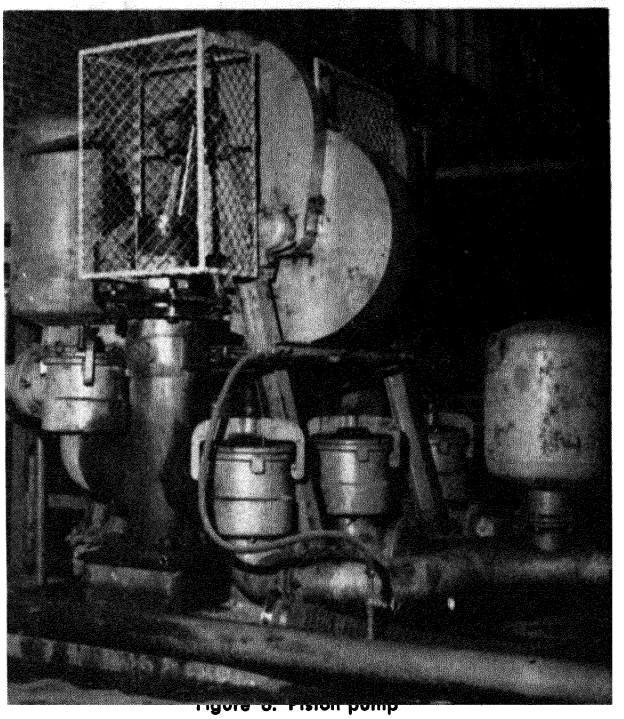

Figure 6. Piston pump

Such a size will certainly also enable a substantial reduction of the production cost, and the present small unit is intended to serve as a full scale experimental plant, where experience is gained for the future industrial requirements in this field.

Some Aspects of the Chemical Treatment of Portuguese Uranium Ores

By F. Videira, P. Marrecas Ferreira and J. D. Almeida,* Portugal

In the field of the utilization of uranium-bearing deposits, Portugal has a tradition that goes back to the beginnings of "radioactivity," the first phase of the recent atomic era.

We were exporting our ores to France as early as 1908, where they were treated in the factory at Nogent. From 1913 to 1926 our country manufactured (Barracao-Guarda Mill) pure salts of radium, radium-bearing barium sulfate, and uranium salts.[1]

For the next 20 years, the activity of our mines and refineries was intermittent and greatly reduced.

This activity was resumed around 1945; its purpose now was the production of uranium concentrates, but there is only one private concern regularly functioning on a genuinely industrial scale.

Profiting by the experience already gained, the Portuguese Commission for Nuclear Energy Studies in collaboration with the Nuclear Energy Committee, has begun to study the question of the chemical concentration and the production of pure uranium oxide on a laboratory scale to determine the optimum conditions in each case.

We feel that by giving some information on our own problems and the general lines we are following in our research in this note, we are carrying out the objectives of this Conference.

The subsoil of European Portugal chiefly contains secondary uranium minerals (autunite, torbernite), plus pitchblende as well all usually associated with small amounts of sulfides (pyrites, galena). The known veins are all in the granitic regions of the Center and the North.

The ores are of various grades but, although the Nuclear Energy Committee is only at the beginning of systematic prospecting, past experience enables us to suppose that normal exploitation of these veins could regularly supply us with raw material having a U_3O_8 content of 0.3–0.6%. There are richer ores.

Our own known ores include many that easily give up their uranium upon treatment with dilute acid or even with water, when the latter has a low pH, upon passing through the pyrites. This circumstance makes possible economical dressing of pure ores by hydro-lixiviation.

In addition to small amounts of lead, copper and arsenic, we usually find 70–80% of SiO_2 (two-thirds of which at least are "free" silica), up to 0.6% (sometimes more) of P_2O_5, and 7–12% of iron and aluminum oxides.

The Boltwood ratio is close to 3.2×10^7.

In most cases the industrial recovery of uranium from these ores requires oxidizing action at the same time.

We must first choose acid or alkali (sodium carbonate) treatment.

Although the latter solution is of interest in certain respects, we feel that treatment with dilute sulfuric acid in the presence of small amounts of an oxidizing agent is preferable (this was not the case for the extraction of radium).

This is, moreover, the method that is required almost everywhere today for these types of ores.

This attack leaves undissolved the Ra (especially in the presence of Ba^{++}), the Pb, and almost all the silica and makes it possible to render 90% or more of the uranium soluble even in the cold.

The principal interfering substances, which partially go into solution, are iron, aluminum and phosphate.

In order to choose the most favorable operating conditions, the following variables should be studied: (1) grain size, (2) temperature, (3) H_2SO_4 concentration of the digesting liquor, (4) ore/solution ratio, (5) percentage of oxidizing agent (generally pyrolusite), and (6) length of digestion.

Actually, the first two factors, which are very strongly dependent on economic factors, should be settled first and will be practically constant. For example, a grain size will be fixed corresponding to passage through 144 mesh/cm^2 screen, and an initial temperature near the ambient. Factor 4 is to some extent linked to 3, but in practice it should be chosen as the maximum value of the ratio, permitting easy stirring and circulation of the sludge and a good subsequent separation, by decantation and filtration, of the solution from the solid phase.

Finally, the study for each type of ore the uranium content of which should not be less than a given value (for example, 0.3% of U_3O_8), is in most cases limited to the effect of: (3) the acid concentration, (5) the percentage of oxidizing agent, and (6) the length of digestion.

These three variables are not independent, but statistical examination of the problem makes it

Original language: French.

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possible to set up procedures under which the number of experiments can be suitably small.

A typical example, for a rich sample, gave us by way of preliminary conclusions: grain size, 144/cm^2; initial temperature, room temperature; solution concentration, 50 gm/l of H_2SO_4; solid/liquid ratio, 1/3 to 1/1 (weight/volume); pyrolusite (65% MnO_2), 2%; recovery (solubilized U), 85–90%.

It should not be forgotten that these are laboratory tests. In order to extrapolate the results to the industrial scale, we must first select the type of apparatus; this is the "chemical engineering" angle. For example, digestion time, a variable of great economic importance, may be reduced in practice by adopting well-designed apparatus. Once the choice has been made, the "transfer" coefficients of results obtained in the laboratory with standard accelerated tests (acid consumption, oxidizing agent consumption, viscosity or fluidity of the sludge, etc.), will be known after a little practice.

We stress the importance of the "chemical engineering" angle; where recent progress makes it possible to hope for new and more profitable ideas, and of industrial operations using "solid-liquid" systems.

Solubilization is the first step in obtaining the concentrate. Two hypotheses arise in our case, both of which have been tried in Portugal, though only one of them on the industrial level.

(*A*) A rich product (>60% of U_3O_8) is wanted. The solution is treated with an excess of Na_2CO_3 (or NaOH + Na_2CO_3) in order to form a uranium complex. This element is then precipitated from the liquid phase by lowering the pH (or by raising it greatly, with NaOH). Generally, sodium uranate is obtained. The technical difficulties involved in this procedure are well known.

(*B*) A relatively lean product will do (20–25% U_3O_8). To achieve this, we raise the pH slightly (6–7), but take care to have as much uranium as possible in the solid phase; hence we precipitate at the same time considerable quantities of aluminum and iron hydroxide and phosphate. This second solution requires closer control but it is undoubtedly cheaper.

We ignore the question of transportation which is of secondary importance by and large if very great distances are not involved.

The concentrate is to be converted into pure oxide, and the way to obtain purification is extraction of solutions of nitrates with a solvent. Consequently, the first step will be to dissolve the concentrate in nitric acid. Some impurities are also soluble, representing useless consumption of acid. This is a strong argument against the type *B* concentrate, which has a percentage of iron, aluminum, calcium, and magnesium oxides and phosphate that may total more than 50%. A Portuguese concentrate with 60–88% of U_3O_8 (type *A*) gave us a total of 11.21% of these impurities upon analysis. To this must be added the Na_2O of the uranate, about 7%, or in other words we still have more than 18% of foreign substances that may be soluble. It would therefore seem that we should concentrate more highly (> 80% U_3O_8), which may be costly if we start with average contents of 0.5, or else we adopt, *as a first stage,* the preparation of a type *B* concentrate, which will give a solution of good purity and rich in uranium after treatment with sodium carbonate. After addition of a suitable amount of nitric acid, the liquid can go into the cycle of extraction with an organic solvent.

The treatment with carbonate will not be expensive. In this case it seems to yield "sludges" that can easily be filtered and represents a purification that is already selective when performed in this phase. Then, by selecting the solvent, we may expect that specific precipitation with H_2O_2 can be eliminated without injury to the purity of the final oxide.

At present, we are examining a solution of this nature, which apparently is being used in other countries. Other methods of concentration will be examined subsequently.

We have already referred to hydro-lixiviation, which is done in Portugal, as a very simple means of treating low-grade ores. The mining section of the Commission for Nuclear Energy Studies is now studying another method: flotation. It is not yet known whether its application to Portuguese industry is urgent.

Obviously, the two possible concentration methods we envisaged are not the only possible ones. Starting with the liquid coming from the solubilization section, a concentrate can be obtained by means other than the classic precipitation after filtration or decantation. Indeed, elimination of the "concentrate" phase is of interest and should be examined.

As for the digestion of these ores, the simplest reagents are used, produced by heavy chemical industry: sulfuric acid, sodium carbonate.

It does not seem, therefore, that this first phase can be improved as for the chemical process itself. As we said, progress should come from the technological side.

However, there will be important changes in the chemical procedure when complex minerals are involved, such as samarskite, euxenite, etc. The same will be true for the treatment of certain raw materials that are very poor in valuable by-products, and are sometimes delicate.

For the time being we have not dealt with the treatment of our complex minerals from Mozambique. For very poor ores and for residues, at the present time, we only contemplate such recovery of uranium as can be effected simply and cheaply.

We are only at the beginning of our task.

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Acid Pressure Leaching of Uranium Ores

By P. M. J. Gray,* Australia

The concentration of uranium from many of its ores is usually effected by hydrometallurgical processes applied directly to the ore itself without prior separation of the uranium-bearing mineral. Less frequently some degree of mechanical separation of the gangue and uranium mineral is practised prior to chemical treatment. The chemical concentration method consists, in outline, of treating the ore, or concentrate, with a solvent to dissolve the uranium as selectively as practicable, separating the solid residue from the liquor and then treating the liquor for the recovery of uranium to give a product containing not less than 80% U_3O_8. The solvents most used are dilute sulphuric acid and sodium carbonate solution but the former is generally preferred unless the ore contains minerals that make the acid consumption excessive. In addition some sort of chemical oxidant must be present during digestion of primary uranium minerals to oxidise the tetravalent uranium to the more soluble hexavalent state. Whilst the ex-works price of the principal reagents used in acid leaching, sulphuric acid and the oxidant, may not be excessively high, the price at a uranium treatment plant in a remote locality may be several times higher. This sort of problem applies, for example, to Australia where distances are great and transport often costly. Consequently consideration has been given to methods of reducing reagent consumption.

The technique of acid pressure leaching provides one way in which reagent consumption may be reduced. In the USA it has recently been shown[1] that sulphide minerals can be oxidised in an aqueous suspension with compressed oxygen at temperatures above about 130°C fast enough to make this an economic proposition for producing soluble sulphates. Ferrous sulphate, for example, thus produced can be oxidised a step further to ferric sulphate which, by hydrolysis, breaks down into an insoluble basic iron compound and sulphuric acid. The sequence of reactions for pyrite can be simply expressed as:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

$$2FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \rightleftharpoons Fe_2(SO_4)_3 + H_2O \quad (2)$$

$$Fe_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Fe(OH_3)\downarrow + 3H_2SO_4 \quad (3)$$

In ores where iron sulphides are associated with uranium minerals these reactions can be utilised to generate sulphuric acid *in situ* for leaching the uranium. In favourable circumstances no acid or chemical oxidant need be added to the leaching vessel; the only reagents required are water and oxygen under pressure. Forward and Halpern[2] have recently published data showing that this has been done on certain Canadian uranium ores.

Acid pressure leaching is also a possible method of reducing reagent consumption in treating ores containing refractory uranium minerals. Minerals which break down only slowly with relatively strong acid under atmospheric conditions may, in some cases, be leached with less acid and in shorter time if digestion is carried out at a temperature of, say 150°C or more.

The ore samples used in this investigation were representative of both types of uranium ore just described. The ore from the Rum Jungle in the Northern Territory contains uraninite associated with iron and copper sulphides and a siliceous slaty gangue and is ideally suited for investigation of *in situ* acid generation. At Radium Hill, in South Australia, the uranium mineral, davidite, is a complex uranium-rare-earth-iron-titanate which requires relatively strong acid to effect decomposition at atmospheric pressure.

Preliminary investigations were carried out on a small laboratory scale in batch type operation. To substantiate the results from the preliminary investigation on the Rum Jungle ore a larger unit treating a continuous ore stream was designed and operated.

LEACHING OF RADIUM HILL CONCENTRATE

Radium Hill ore is amenable to physical concentration and the tests described here were carried out on such a concentrate. The composition of davidite precludes, however, the preparation of a concentrate sufficiently rich in uranium.

In devising a new method of leaching this concentrate two specific improvements are desirable: (*a*) a means of reducing acid consumption; (*b*) a means of producing a liquor containing less iron and titanium which may be particularly troublesome during subsequent treatment.

Typical results obtained in conventional leaching of davidite concentrates at atmospheric pressure are summarized in Table I. These results were obtained by treating a concentrate containing 0.7% U_3O_8 and ground to − 150 + 200 mesh. Eight hours' digestion was used.

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Table I. Leaching of Radium Hill Concentrate at Atmospheric Pressure and 100°C

*Acid used lb/ton**	*Pulp density % solids*	*U_3O_8 extraction*	*TiO_2 concn., of liquor gm/l*	*Fe_2O_3 concn., of liquor gm/l*
610	45.5	89.5	0.37	>50
765	40.0	91.2	0.66	>50
920	35.7	92.3	0.68	>50
920	45.5	91.8	1.06	>50

* Acid concentrations throughout this paper are expressed as pounds of 98% H_2SO_4 per short ton (2000 lb) of ore.

These results show that to get satisfactory uranium extractions (>90%) relatively large amounts of acid must be used but that at the same time the iron and titanium concentrations in the liquor are higher than desirable for subsequent operations.

The pressure leaching tests were carried out with 25.0 gm of concentrate pulped with 25.0 cm^3 of dilute acid. The autoclave had a capacity of 330 cm^3 and was rotated on an inclined axis during digestion to stir the pulp. An internal baffle further aided mixing and aeration. Before being heated the autoclave was loaded with oxygen under pressure to provide an oxidant for the iron in solution and thus promote removal of iron by hydrolysis. A resistance winding round the autoclave was used to heat it.

In the pressure leaching tests the amount of acid and length of time were varied. The temperature in each test was 150°C and the total working pressure about 100 psig. Results are summarized in Table II.

Table II. Pressure Leaching of Radium Hill Concentrate

Acid used lb/ton	*Time hr*	*Extraction of U_3O_8 %*	*TiO_2 conc. of liquor gm/l*	*Fe_2O_3 conc. of liquor gm/l*
205	3	63.0	<0.05	0.70
205	6	73.6	<0.05	0.60
306	3	86.9	<0.05	3.05
306	6	94.7	<0.05	2.85
306	6	90.3	<0.05	3.12

The best uranium extractions in these tests were as good as or better than, those obtained in non-pressure leaching using only a third as much acid and in less time. Furthermore the titanium concentrations were greatly reduced as were the soluble iron concentrations.

LEACHING OF RUM JUNGLE ORE

The main purpose of the tests on Rum Jungle ore was to discover whether enough acid could be generated *in situ* to get uranium extractions comparable with those obtainable under atmospheric conditions. The tests were also designed to find what the optimum conditions for leaching were.

Table III. Chemical and Screen Analyses of Rum Jungle Ore Sample

Chemical	*Per cent*	*Screen B.S.S. mesh*	*Per cent*
U_3O_8	0.47	−44 + 60	18.0
Cu	2.71		
S	3.00	−60 + 100	10.0
Fe	4.0	−100 + 150	10.2
Al_2O_3	22.8	−150 + 200	2.5
SiO_2	52.7	−200	59.0

The chemical and screen analyses of the ore sample used are given in Table III.

Typical uranium extractions from the ore sample in cold atmospheric leaching are given in Table IV. The ore samples were treated at 50% solids in the presence of 3% MnO_2 as an oxidant. Time of digestion was twenty-four hours.

Table IV. Leaching of Rum Jungle Ore at Atmospheric Pressure

Acid used lb/ton	*U_3O_8 extraction, %*
153	89.0
205	90.6
306	92.8

Pressure leaching tests were carried out in like manner to those on the Radium Hill concentrate except that the ore was pulped at 50% solids with water instead of dilute acid. The effect of four controllable variables, time, temperature, oxygen partial pressure and degree of grinding, upon the uranium extraction was studied independently. The amount of soluble copper and sulphate produced, the iron concentration and the pH value of the liquor were also noted in each run. These results are summarised in Tables V to VIII.

The relatively high uranium extraction at nil oxygen partial pressure is probably attributable to the presence of some sulphate in the original ore sample. Theoretically only 1.7% of the sulphur in the ore need be converted to, or present as, sulphate to provide for the solution of all the uranium, as uranyl sulphate. In practice, of course, more is required due to the consumption of sulphate by other soluble minerals. Most of the iron in the liquors was in ferrous form; in the first run entirely ferrous.

The lower uranium extractions obtained with the most finely ground material were believed to be due to the viscous nature of the pulp which prevented adequate stirring and aeration. It appears that ore of the screen analysis given in Table III is near to the optimum physical condition for pressure leaching.

In most of the tests listed in Table V to VIII uranium extractions appreciably better than those

Table V. Effect of Variations in Oxygen Partial Pressure in Pressure Leaching Rum Jungle Ore Temperature: 140°C; Time: 2 hours

Oxygen partial pressure psi	*U_3O_8 extraction %*	*Cu extraction %*	*Percent of S converted to $SO_4^=$*	*Fe_2O_3 conc. in liquor gm/l*	*pH of liquor*
nil	29.0	nil	6.8	2.18	3.78
40	80.5	22.6	19.1	1.08	1.86
80	90.1	43.6	31.5	1.69	1.72
140	94.3	56.4	41.2	1.62.	1.56
200	98.0	57.9	41.7	1.30	1.76

Table VI. Effect of Variations in Temperature in Pressure Leaching Rum Jungle Ore. Oxygen Partial Pressure: 140 psi; Time: 2 hours

Temperature °C	U_3O_8 extraction, %	Cu extraction, %	% of S converted to SO_4 =	Fe_2O_3 concentration in liquor gm/l	pH of liquor
100	47	19.9	13.1	Not detected	3.65
140	94.3	56.4	41.2	1.61	1.56
180	98.6	87.1	74.6	0.90	1.09
200	98.5	86.5	76.4	0.60	1.23

Table VII. Effect of Variations in Time in Pressure Leaching Rum Jungle Ore. Temperature: 180°C; Oxygen Partial Pressure:140 psi

Time hr	U_3O_8 extraction, %	Cu extraction, %	% of S converted to SO_4 =	Fe_2O_3 concentration in liquor gm/l	pH of liquor
0.5	93.0	43.5	35.6	1.60	1.49
1.0	95.3	60.0	37.4	1.50	1.25
2.0	98.6	87.1	74.6	0.90	1.09

Table VIII. Effect of Variation in Degree of Grinding in Pressure Leaching Rum Jungle Ore. Temperature: 140°C; Oxygen Partial Pressure: 120 psi; Time: 2 hours

Degree of grinding	U_3O_8 extraction, %	Cu extraction, %	pH of liquor
(21.5% −14 + 44 mesh (51.4% −200 mesh	85.2	40.5	1.73
100% −¼ in.+ 14 mesh	33.1	10.6	2.30
As in Table III	91.3	42.7	1.70
As in Table III	95.3	56	1.25
Ball milled extra two hours	92.1	59.5	1.41
Ball milled extra 12 hours	86.4	28.0	1.63

obtained in cold leaching were achieved without adding any acid at all. Nor was any oxidant apart from compressed oxygen, required. Other ways in which these results showed improvement over cold leaching were:

(*a*) The leaching was much more rapid. Better uranium extractions were obtained by leaching at 180°C for 30 minutes than were obtained in 24 hours by cold leaching.

(*b*) The leaching was more selective with respect to impurities like iron and aluminum. The ignited ammonia precipitate from a cold leach liquor normally contains only 25-30% U_3O_8 whereas from a pressure leach liquor it contains about 50% U_3O_8.

(*c*) The degree of grinding required is less. Up to 93% of the uranium can be extracted in cold leaching if the ore is ground to 80% −200 mesh but better extractions than this could readily be obtained in pressure leaching when only about 60% of the ore was −200 mesh.

These results showed that high uranium extractions were attained either at 140°C in two hours digestion or at 180–200°C in only one hour. Since an oxygen pressure of 120–140 psi was used in each case the total working pressure would be lower at the lower working temperature. However, if equally good extractions could be achieved at 180–200°C at a much lower oxygen pressure, working pressures would be comparable. To see whether this could in fact be done, two further runs were carried out and the results are summarised in Table IX.

Table IX. Effect of Variations in Oxygen Partial Pressure at 200°C in Pressure Leaching Rum Jungle Ore. Temperature: 200°C; Time: 1 hour

Oxygen partial pressure psi	U_3O_8 extraction %	Cu extraction %	Percent of S converted to SO_4 =	Fe_2O_3 conc. of liquor gm/l	pH of liquor
35	89	10.6	27.9	1.55	1.52
55	96	26.9	40.8	1.90	1.04

The total working pressure used in these tests was 200–250 psig which is approximately the same as that required to get high uranium extractions at 140°C. However, if the equivalent working pressures be computed when air is used under the same conditions it is found that the total pressure at

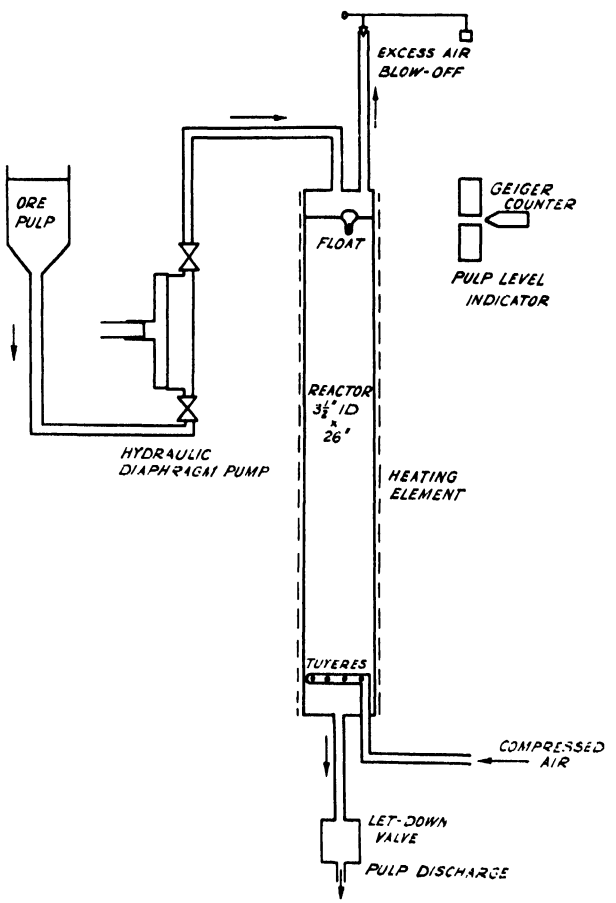

Figure 1

200°C will be about 410 psig and at 140°C about 650 psig. Since also at the higher temperature the rate of leaching is twice as fast, it was considered that the conditions of 180–200°C and an oxygen partial pressure of 40–45 psi were the more advantageous.

CONTINUOUS PRESSURE LEACHING REACTOR

The above tests on Rum Jungle ore were carried out under rather limited conditions; for example, the the oxygen pressure was not maintained by constant replenishment, the pulp was not efficiently aerated and some leaching undoubtedly occurred during the heating-up period which is not included in the recorded times. To enable data to be collected under conditions which were not so limited a small reactor was built capable of treating about two kilograms of ore per hour with both the ore pulp and the oxidising gas fed in continuously. The principle of this reactor is shown diagrammatically in the accompanying sketch. The plant was designed to operate at temperatures up to 200°C and total pressures up to 500 psig. It consisted of a mild steel shell lined with stainless steel (titanium stabilized austenitic)with all ancillary equipment made of the same stainless steel. No corrosion trouble has been experienced and this is thought to be due to the relatively low free acidities combined with oxidising conditions and possibly also the inhibiting effect of dissolved copper. The pulp is agitated and aerated by air injected through an annular tuyere. There are no moving parts within the reactor and the pulp is not agitated vigorously enough to cause abrasion of the lining. The composition of the pulp throughout the reactor was constant so that fresh pulp entered a system that was already hot and acid. Under these conditions the retention time of the pulp in the reactor was only an average one but nevertheless leaching was found to be more rapid than in batch operation. The pulp level in the vessel was indicated by a radioactive Co^{60} source in a glass float whose position could be located with an external Geiger counter placed behind a horizontal slit in a lead shield.

In this reactor Rum Jungle ore has been treated so that more than 95% of the uranium was leached in a retention time of only 50 minutes at 180°C and an oxygen partial pressure of 40 psi (total working pressure about 370 psig). These results compare more than favorably with those obtained in the preliminary series of tests and help to fulfill further the promise that this technique shows for treating certain uranium ores.

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The South African Uranium Industry

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HISTORICAL DEVELOPMENT OF SOUTH AFRICAN URANIUM INDUSTRY

The first published reference to the existence of uranium in the gold ores from the Witwatersrand series of conglomerates was made by R. A. Cooper in a paper read before the Chemical, Metallurgical and Mining Society of South Africa in October, 1923.

In 1922, the Central Mining-Rand Mines Group, which at that time was responsible for the milling of 49% of the total ore being milled on the Witwatersrand, decided to change over from plate amalgamation to corduroy concentration for the recovery of the free gold in the ore. The primary reasons for this change were to lessen the mercurial poisoning hazard and the theft hazard and to reduce the consumption of mercury. The change-over to corduroy on the sixteen large gold producers of the Group was carried out during 1922 and 1923.

A result of the change was that the amount of concentrate collected daily was in excess of the capacity of the amalgamation barrels and it was therefore decided to reconcentrate the corduroy concentrate on reciprocating tables. An examination of the products on these tables revealed the presence of considerable quantities of osmiridium and steps were immediately taken to recover as much of this osmiridium as possible. The net result was that, whereas the osmiridium recovery for the Witwatersrand was 510 oz in 1921, it rose to 5764 oz in 1924.

During this investigation the presence of minerals not previously observed in Witwatersrand concentrates was noticed on the Wilfley tables during reconcentration and samples of these minerals were taken to the Rand Mines Laboratory where analyses were carried out, which resulted in establishing the existence of uranium in Witwatersrand ores. A photograph, hitherto unpublished, is shown hereunder, which illustrates the radioactivity of products obtained from the samples submitted to the Rand Mines Laboratory.

The significance of the existence of uranium in Witwatersrand ores was not appreciated until about 1944 when a world-wide search was instituted to find the raw materials which were required for the manufacture of atomic bombs.

Early in the Second World War the United States and the United Kingdom Governments formed a "Combined Development Agency," whose chief function was to find uranium for both of these countries for the production of nuclear energy.

In 1944, an American geologist, Weston Bourret, visited the Witwatersrand when on his way to Madagascar, and he submitted a secret report to the United States Government on the occurrence of uraninite in amalgamation barrel residue. This led Dr. G. W. Bain, Professor of Geology at Amherst College, Massachusetts, and consultant to the United States atomic bomb undertaking, the Manhattan Project, to make a radiometric examination of two specimens of Witwatersrand ore in his possession, which confirmed the presence of radioactive minerals in these ores. He made a secret report to the combined American and British Authorities and, as a result, these two Governments approached the South African Government in 1945 about the possibility of extracting uranium from Witwatersrand gold ores. At the same time, Dr. Bain and Dr. C. F. Davidson, Chief Geologist of the Atomic Energy Division of the Geological Survey of Britain, visited South Africa.

The first quantitative assessment of the uranium potentialities of the Witwatersrand goldfield in the light of modern requirements was made by these two men and Dr. Davidson's report in October, 1945, to the Department of Scientific and Industrial Research in London ended with these significant words:

> "Present evidence appears to indicate that the Rand may be one of the largest low-grade uranium fields in the world."

The findings of Bain and Davidson indicated that the uranium in Witwatersrand ores was many times more plentiful than gold.

The South African Government, with Field-Marshal Smuts as Prime Minister, took the keenest interest in the uranium developments and the Prime Minister informed the President of the Transvaal Chamber of Mines that this was a matter of vital importance to South Africa. He stated that the Government desired to ascertain the magnitude of the Witwatersrand uranium deposits and how these deposits could best be developed. The whole-hearted support of the Gold Mining Industry was pledged.

The Prime Minister set up a Uranium Research Committee, with Dr. B. F. Schonland as Chairman, and on which were represented the Gold Mining Industry, the Department of Mines, the Department

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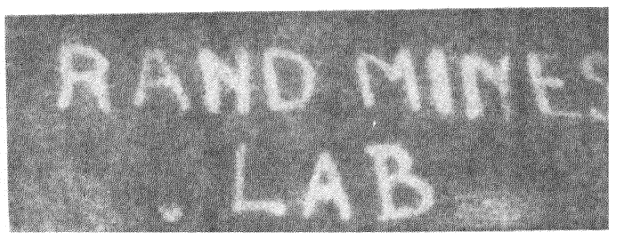

Figure 1

of External Affairs and the Geological Survey. The work of this Committee was helped by various sub-committees, one of which was the Geological Sub-Committee. The chief task of this sub-committee was to value the uranium potential of every producing and developing gold mine and to evaluate samples from all boreholes. In the course of this work, over 400,000 samples sent forward by the various mining companies to the Geological Survey were tested for uranium by Geiger-Müller counter. Thus were the potentialities of the mines assessed.

A Government Metallurgical Laboratory Technical Sub-Committee comprising four members was also formed to assist the Uranium Research Committee. This sub-committee was expanded in October, 1946, and comprised the Government Mining Engineer as Chairman, the Director of the Government Metallurgical Laboratory, Dr. B. F. Schonland, one member of the Gold Producers' Committee of the Chamber of Mines, six of the Gold Mining Industry's senior Consulting Metallurgists and one Consulting Electrical and Mechanical Engineer from the Industry. This sub-committee started an investigation at the Government Metallurgical Laboratory (G.M.L.) into methods of treating South African ores for uranium recovery.

Similar research programmes were initiated at the Chemical Research Laboratory at Teddington, England, and at the Massachusetts Institute of Technology (M.I.T.) and elsewhere in the United States of America and all reports from overseas on South African ores were made available to the Government Metallurgical Laboratory Technical Sub-Committee.

Dr. Schonland and the Director of the Government Metallurgical Laboratory visited Britain and the United States of America at the end of 1946 and Dr. Bain and Dr. Davidson again visited the Union in 1947 at the same time as Dr. A. M. Gaudin of M.I.T. Thus a close liaison was maintained between the overseas investigators and the G.M.L. Technical Sub-Committee.

To facilitate research work at the G.M.L. it was necessary to second thereto a number of employees of the Gold Mining Industry.

Initial research at the G.M.L. was directed toward gravity and flotation concentration with the purpose of reducing the tonnage that would otherwise require to be leached with sulphuric acid to permit the recovery of uranium therefrom. By means of flotation plus acid leaching of the flotation concentrate it would have been possible to recover uranium at a lower cost per pound but there would have been a considerable reduction in the amount of uranium recovered. However, the G.M.L. Sub-Committee was informed by higher authority that maximum output was the vital issue, notwithstanding the increased cost thereof, and consequently the Sub-Committee was directed toward acid leaching of the total ore. Satisfactory extractions were obtained by this method on ores submitted by many mines to the G.M.L. and it was then decided to erect two pilot plants, one at Blyvooruitzicht and the other at Western Reefs, both of which mines appeared to be certain to become uranium producers, provided a satisfactory price for the uranium could be negotiated. These pilot plants were started up in October, 1949, and February, 1950, respectively, and were kept in operation until 1953 when these mines did, in fact, become large uranium producers.

In the meantime, research work was continued at the G.M.L. and by the end of 1950 sufficient information was available to permit the recommendation of a satisfactory metallurgical flow-sheet for uranium recovery from Witwatersrand ores, with sufficient data to indicate likely recoveries and probable cost of recovery. Moreover, information was available as to which were the most promising potential uranium producers.

In May, 1948 there was a change in the South African Government and Dr. D. F. Malan succeeded Field-Marshal Smuts as Prime Minister. The new Government displayed the same keenness as the previous Government to make South Africa a leading uranium producer.

In September 1948, the South African Atomic Act was promulgated. This Act, which was amended by Act No. 8 of 1950, reserves to the State the ownership of "prescribed materials" as well as the right to prospect and mine for them. "Prescribed material" is defined in Government Gazettes of the 10th March, 1950, and the 28th July, 1950, as any substance containing more than 0.006 per cent U_3O_8 —equivalent to 0.12 lb or 1.75 troy oz per ton— or more than 0.5 per cent ThO_2. The Act enables the State to grant authority for the mining and extraction of prescribed materials. The Act also provided for the formation of the Atomic Energy Board which is the body which, on behalf of the South African Government, deals with all matters relating to uranium.

In November 1949, at the invitation of the Union Government, representatives of the United States Atomic Energy Commission and the Government of the United Kingdom arrived in South Africa to discuss problems relating to the production of uranium.

Discussions took place between the mission and representatives of the South African Government and the Gold Mining Industry, but these were solely of an exploratory nature and no finality was reached in these talks. It was, however, decided that the

mission would return towards the end of 1950 and at similar talks in November and December 1950, agreement was reached to the effect that South Africa would undertake to produce uranium oxide for sale to the Combined Development Agency.

The agreement was along the following lines:

1. The Atomic Energy Board would grant authority to approved applicants to mine and produce uranium.

2. The capital required to install uranium plants and pyrite recovery and sulphuric acid plants required by the uranium industry would be loaned by the purchasers of the uranium output, subject to the repayment of these loans during the ten-year period of the purchasing contract.

3. The required uranium output for the ten-year contract was agreed and the purchasers were given the first refusal of any amounts in excess of that quantity.

4. Production should be commenced with the least possible delay.

5. The selling price of the uranium oxide was related to the cost of production, including an allowance for amortisation of the capital cost of the plant, in such a way that there was an incentive to the producer to keep working costs as low as possible. It was calculated that the selling price would ensure a reasonable margin of profit to the producer.

6. In establishing the price formula, cognisance was taken of the fact that the South African Government had made it clear that all uranium profits, like profits by the Gold Mining Industry from the recovery of silver and osmiridium, would be combined with the gold mining profits of the producing company and be subjected to taxation on the same basis as the profits from gold. On the other hand, it was also made clear that amortisation of the capital expenditure on account of uranium would be permitted by the South African Government on exactly the same basis as capital expenditure in gold mining.

7. The recovery of uranium was to be considered essentially a by-product recovery and was not in any way to affect adversely the recovery of gold.

8. To minimise health hazards, the final product would be taken from each mine in the form of a wet slurry and be delivered to a central works where it would be dried, calcined and sampled prior to being packed in drums and shipped overseas.

9. The Sellers were to maintain secrecy concerning the extraction process, the terms of the contract relating to price, the grades of ore treated, the rates of extraction and the tonnages and destination of the product to be delivered.

The 1950 agreement provided for uranium production by only four mines but by the end of 1951 the urgency of stepping-up uranium output was so pressing that the Combined Development Agency made an approach to the Atomic Energy Board and asked that the South African output be increased very materially. The Board agreed to this proposal, which necessitated bringing many more gold mines into the uranium industry. At the same time, it was agreed that the selling price formula would be amended whereby a higher price per lb of U_3O_8 would be paid to all South African producers.

The foregoing terms apply with little change at the present time, and the approved uranium producers and the location of the uranium plants (as at the end of April, 1955 and April, 1956) are shown in Table I.

Table I discloses that, in terms of the foregoing programme, 26 mining companies have been accepted as uranium producers and that the ores from these companies will be treated in 15 uranium plants.

OCCURRENCE AND DISTRIBUTION OF URANIUM IN WITWATERSRAND ORES

The gold ores of the Witwatersrand exist as thin layers of conglomerate, locally known as "reefs," separated from each other by interbedded quartzites or shales, which form part of the Witwatersrand series of sediments.

The ore-bearing reefs are made up of closely packed rounded quartz pebbles, set in a mineralized quartzitic matrix, which carries the valuable constituents comprising gold, silver, osmiridium, pyrites, uranium and, on rare occasions, diamonds. The pebbles themselves and the beds of quartzite and shale between the reefs are virtually barren of valuable mineral.

Uranium occurs in the matrix of the conglomerate as free grains of uraninite, of which the major constituents are oxides of uranium. Sometimes the uraninite is closely associated with or embedded in a carbonaceous material which could be described as a variety of the hydrocarbon thucholite with relatively low thorium content. Thucholite is a hydrocarbon of variable composition containing variable amounts of thorium, uranium, carbon, oxygen, hydrogen, rare earth oxides and silica, and its name is derived from the first four of these elements.

There is no close association between pyrite and uraninite in Witwatersrand ores. There is, however, in individual mines, an apparent association between gold and uraninite but this is probably merely coincidental because of the association between gold and carbon on the one hand and uraninite and carbon on the other. For example, in some mines high uranium values are found with high gold values, and vice versa. However, other mines may, on the average, have relatively high gold values associated with low uranium values and still other mines may have relatively low gold values and high uranium values.

Uranium is found in virtually all of the Witwatersrand reefs but, in some areas, such as that from Roodespoort in the near West to Springs in the near East Rand, the uranium contents of the gold ores already mined, or to be mined, are unlikely to be high enough to make its extraction an economic proposition. Thus the vast deposits of sand and slime residues existing in that area are likely to be worthless from the uranium aspect.

Table I. Approved Uranium Producers

Mining company	*Location of uranium plant*	*Date of commencement of plant*
West Rand Consolidated Mines, Ltd.	West Rand Cons.	October, 1952
Daggafontein Mines, Ltd.	Daggafontein	April, 1953
Blyvooruitzicht G.M. Co., Ltd.	Blyvooruitzicht	April, 1953
Western Reefs Expl. and Dev. Co., Ltd.	Western Reefs	September, 1953
Stilfontein Ellaton Afrikander Lease New Klerksdorp Babrosco	Stilfontein	September, 1953
Randfontein Estates G.M. Co. W., Ltd. East Champ d'Or G.M. Co., Ltd.	Randfontein	February, 1954
Luipaards Vlei Estate and G.M. Co., Ltd.	Luipaards Vlei	November, 1954
Vogelstruisbult G.M. Areas, Ltd.	Vogelstruisbult	December, 1954
President Steyn G.M. Co., Ltd. President Brand G.M. Co., Ltd. Free State Geduld Mines, Ltd. Western Holdings, Ltd.	President Steyn	January, 1955
Welkom G.M. Co., Ltd. Freddies Consolidated.	Welkom	January, 1955
Harmony G.M. Company, Ltd.	Harmony	March, 1955
20 companies	11 uranium plants	as at April, 1955
Dominion Reefs (Klerksdorp) Ltd.	Dominion Reefs	June, 1955
Virginia O.F.S. G.M. Co., Ltd. Merriespruit (O.F.S.) G.M. Co., Ltd.	Virginia	September, 1955
West Driefontein G.M. Co., Ltd. Doornfontein G.M. Co., Ltd.	West Driefontein	March, 1956
Vaal Reefs Expl. and Mining Co., Ltd.	Vaal Reefs	March, 1956
26 companies	15 uranium plants	as at April, 1956

The Main Reef series of the Witwatersrand system, from which the bulk of the Witwatersrand gold output has been obtained to date, are not the only reefs in the Witwatersrand geological system. Many other reefs exist above and below the Main Reef series (mostly above) and these other reefs are likely to prove more important as uranium carriers than the Main Reef series.

Starting from the upper strata of reefs, from which uranium is being or will be recovered and descending downwards, the first are the Elsburg Reefs from which the Western Reefs mine is recovering uranium. Next are the Kimberley Reefs from which Daggafontein and Vogelstruisbult are extracting uranium. Then comes the Bird Reef series, including the Monarch Reef and the White Reef, relatively low in gold content but high in uranium values, from which East Champ d'Or, Luipaards Vlei, West Rand Consolidated and Randfontein Estates are recovering uranium. The gold content of this series is generally insufficient to cover the costs of gold mining and gold recovery, but the uranium content will be responsible for the mining of large tonnages of ore which otherwise would be left unworked. The Monarch Reef also appears in the Klerksdorp district under the name of the Vaal Reef and in the Orange Free State under the name of the Basal Reef. Uranium is being recovered, or will be recovered, from these reefs by Stilfontein, Vaal Reefs, New Klerksdorp, Ellaton, Western Reefs, Freddies Consolidated, Welkom, Western Holdings, President Steyn, President Brand, Free State Geduld, Harmony and Virginia.

Then come the unimportant Livingstone and Johnstone reef zones and then the Main Reef series of which the carbon leader at the bottom of the series is, from the uranium point of view, the most significant. This is being worked for gold and uranium by West Driefontein, Blyvooruitzicht and Doornfontein on the Far West Rand.

Below the Main Reef series is the Government reef zone, which is worked in its upper formations for uranium at Babrosco and at Afrikander Lease Areas.

Then comes, as the lowest of all the reefs, the Dominion Reef series worked for uranium only by the Dominion Reefs mine.

On some mines, such Blyvooruitzicht and Western Reefs, which in the past have milled large tonnages of gold ore which was deposited after treatment in residual slime dams, these dams are being reclaimed and treated with current ore for uranium recovery. On other mines, such as Daggafontein and Vogelstruisbult, there are residual slime dams with relatively low uranium content but these dams are also being reclaimed and subjected to the flotation process by which means a concentrate, relatively high in uranium value, is recovered and treated with current ore in the uranium plants. At Merriespruit the whole of the current residue from the gold recovery section will be floated to give a

uranium concentrate which will be treated in the Virginia uranium plant.

On some gold mines which currently mine different reefs, it has been possible to keep the ores which are relatively high in uranium content entirely separate from ore relatively low in uranium content by treating the latter in a separate section of the gold plant or in an entirely separate gold plant and then passing only the gold residues relatively high in uranium content into the uranium plant. Vogelstruisbult, Daggafontein, Luipaards Vlei, West Rand Consolidated and Randfontein fall into this category.

The uranium industry remains secondary to the gold industry in South Africa and consequently, with the exception of the near West Rand area, it is the gold content of the ore which primarily decides whether or not it shall be milled. Since the uranium plants have to take whatever ore passes through the gold plant there is, with the exception of the near West Rand area, no close control of uranium values entering the uranium plants.

SOUTH AFRICAN URANIUM METALLURGICAL PRACTICE

Before the advent of the uranium industry, the residues from the gold plants were pumped to slime dams for storage. The solids delivered to these dams were accompanied by at least their own weight of a cyanide lime solution containing some gold in solution. This solution settled out on the dams and about one-third of the total solution was reclaimed by decantation and returned to the gold plant where the cyanide and lime were reused and portions of the gold recovered.

With the advent of the uranium plant it became necessary to pass the residue from the gold plant straight into the uranium plant and, in order to recover some of the cyanide, lime and gold which would otherwise be lost, it was decided in most cases to filter the gold plant residue on non-acid rotary filters and to return the gold and cyanide solution therefrom to the gold plant. These filters serve the further purpose of removing as much lime and cyanide as possible from the residue before it comes into contact with sulphuric acid solution thereby reducing the acid consumption in the uranium plant and removing the danger of the generation of prussic acid gas. They also serve to remove salts such as cobalticyanide which if allowed to pass into the uranium plant would cause trouble therein. These filters are also essential to dewater slime which has been reclaimed by hydraulicing old slime dams, prior to passing the slime therefrom into the uranium plant. In a few cases, where cyanide strengths in the gold plant are relatively low, non-acid filters have been omitted.

The process of uranium extraction is basically similar to that employed in the recovery of gold. It can be divided into the same three stages, dissolution, separation of the solution containing the dissolved valuable constituent from the impoverished solids and the recovery of the valuable constituent from the solution. In one case, however, alkali solutions which have no adverse effect on mild steel are used whereas, in the other, acid solutions are used which require rubber-lined mild steel vessels or the use of acid-resisting steel.

The dewatered residue entering the uranium plant is re-pulped with dilute sulphuric acid solution which is the filtrate from the secondary acid filtration stage (see later) and is then pumped into large rubber-lined tanks 22½ ft in diameter and 45 ft tall. To these tanks, the requisite amount of strong sulphuric acid is added, together with ground manganese dioxide ore. The pulp in these tanks is agitated by means of compressed air for about 16 hours in which time the major portion of the uranium goes into solution. For satisfactory dissolution it is necessary to have ferric sulphate present in addition to free sulphuric acid. The ferric sulphate is obtained from free metallic iron in the ore which owes its origin to the wearing of steel balls and cylindrical mill linings used in the grinding plant of the gold section. This iron is attacked by the sulphuric acid and ferric sulphate is formed in the presence of the oxidising agent (MnO_2), assisted to a minor degree by the air used in agitation. Dissolution is improved by applying heat and, in at least one plant, steam injected into the agitation tanks.

The next stage is the separation of the uranium solution from the treated slime and for this purpose acid-resisting canvas covered rotary filters are used. However, the filtration of the pulp is difficult and a filtration aid, in the form of liquid glue, is added to each agitator just prior to gravitating the pulp therefrom to the primary acid filters. At the present time tests are being carried out with synthetic filter-aids to take the place of, or to reduce the use of, glue. The filtrate from these filters is pumped to the recovery section (see later) and the residue cake which still carries some of the dissolved uranium is repulped with acidified water and is pumped to a second similar set of agitators in which it is retained for about five hours before being gravitated to a secondary similar set of acid-resisting rotary filters. The residual cake from these filters is repulped and discharged to the residue dam or to a flotation plant for the recovery of pyrite therefrom prior to discharge to the residue dam. The filtrate is used, as already indicated, to repulp the residual cake from the non-acid filters.

The uranium-bearing solution delivered to the recovery section is clarified by being passed through sand filter beds and it is then passed through columns wherein the uranium with a relatively small amount of iron is retained and the effluent sulphuric acid solution, devoid of uranium but containing a considerable quantity of iron sulphate and manganese sulphate, is passed on to the manganese recovery section.

The uranium and iron retained in the recovery columns are periodically removed therefrom with a

solution containing a mixture of nitric acid and nitrate salts, and the iron is removed from this solution by raising the pH to 3.7 by the addition of milk-of-lime. The precipitated iron hydroxide is settled in a thickener and the underflow therefrom is filtered on a rotary filter and the cake, containing some uranium, is delivered back to the primary acid agitators for re-dissolution. The filtrate from this filter and the overflow from the thickener are then treated with ammonia and ammonium diuranate is precipitated at a pH of 6.9. This precipitate is collected in a thickener and the underflow therefrom is filtered to give the final product containing the uranium output. The filtrate from this filter and the overflow from the thickener are brought back to nitrate strength and reused to extract uranium from the recovery columns.

The final product, ammonium diuranate $(NH_4)_2U_2O_7 \cdot 3\,H_2O$ is despatched in wet form to a central calcining works where it is dried and calcined to U_3O_8 and sampled prior to packing in steel drums for despatch overseas to wherever the buyer directs.

In the manganese recovery section the acid effluent from the uranium recovery columns is agitated with ground limestone to raise the pH to 4.5 when the iron is precipitated, thickened, filtered and discharged to the slime dam. The clear thickener overflow and the filtrate from the filter are then agitated with milk-of-lime to raise the pH to about 9.0, when the manganese is precipitated and the mixture is then passed into a thickener from which the clear overflow, virtually water, is used to discharge residues to the slime dam and the underflow, containing the manganese in the form of hydroxide is pumped to storage dams where it oxidises further to form MnO_2 which is later returned to the uranium plant. The recovery of manganese in this way is expected to amount to about 50% of the total manganese dioxide requirements in the uranium plant.

The uranium plant is equipped with considerable subsidiary equipment such as grinding mills for limestone and manganese ore, chemical storage plant, laboratory, offices, etc.

THE LAUNCHING OF THE SOUTH AFRICAN URANIUM INDUSTRY

The advent of the uranium industry coincided with a period of remarkable mining and industrial activity in South Africa. Electric power was in short supply; likewise steel plate and sections. Large quantities of chemical reagents, such as sulphuric acid, lime, limestone, nitric acid, ammonia and glue would be required. The cost of an average uranium plant was known to be of the order of £3,000,000 and it was obvious that the resources of the country would be strained. However, it was decided that the uranium plants must be built and operated and, in order not to affect adversely the gold mining industry, it was decided that, if necessary, materials should be imported from overseas for the uranium industry. It was realised that the early production of uranium was vital and the gold mining industry decided to make an extreme effort to get the undertaking into production with the least possible delay. Consequently it was decided that this project should be dealt with on the highest level and the most experienced personnel in the Gold Mining Industry were called upon to bring the uranium project into being.

To illustrate the vastness of the project, the chemical reagents which are required for the present uranium programme are approximately as follows (in tons per month): sulphuric acid (100%), 39,000; burnt lump lime (90% CaO), 15,000; limestone (96% $CaCO_3$), 10,000; manganese ore (40% MnO_2), 18,000; glue (solid), 400. Large quantities of nitric acid and ammonia are also used. The electric power requirements are 77 megawatts and the water requirements are of the order of 300 million gallons per month.

As soon as agreement was reached at the end of 1950 for the production of uranium, the Chamber of Mines put its services at the disposal of the uranium industry. Whilst each mining group interested in the production of uranium was individually capable of developing its own process and designing its own production plants, it was obvious that a co-operative effort could achieve these things more expeditiously and indeed, in this case, more satisfactorily.

Gold mining has always operated on a non-competitive basis and, through the Chamber of Mines, the Industry had built up a system of joint consultation and co-operation which was of great value to the gold mining industry. The availability of this same co-operation was an important factor in the success attained in achieving remarkably early uranium production.

At the end of 1950 the Chamber of Mines established the Uranium Technical Sub-Committee, consisting of the Chief Consulting Electrical and Mechanical Engineers and the senior Consulting Metallurgists of the Groups directly interested in uranium production. The function of this Committee was to investigate ways and means of achieving early uranium production and to report accordingly to the Executive Committee of the Chamber. It was decided also to set up a Uranium Department in the Chamber under the direction of a highly qualified metallurgist. This Department was of the greatest assistance to the Uranium Technical Sub-Committee.

The Uranium Technical Sub-Committee designed the flow-sheets for the uranium plants and this was the first time in the history of the Gold Mining Industry that a committee of the Chamber had assisted individual mines in this way. Of course each mine was ultimately responsible for its own installation.

The Sub-Committee also studied acid-resisting materials, it recommended standardization of sizes of units, etc., it explored the manufacturing potentialities of large and small South African engineering and building companies, it investigated the availability of raw materials and it assumed the responsibility of acquiring these on an Industry basis

through the Chamber of Mines Stores Sub-Committee.

The Technical Sub-Committee investigated the electric power position; it took steps for bulk ordering of steel from overseas. It investigated the carrying capacity of the railways and in fact it did everything to expedite uranium production. That the Sub-Committee achieved its task admirably is proved by the fact that within twenty-one months of the decision being made to install large uranium plants, the first was in production, followed by two others six months later. Many overseas visitors have expressed amazement at these achievements. On the other hand, however, the Industry was amazed also at the expeditious way in which delivery of material to the project was made, due largely to the extremely high priority given by all of the three Governments directly concerned with the South African production of uranium. The South African Railways have also served the industry well. It can safely be said that no major industry in the history of South Africa has been developed as rapidly as the uranium industry.

Initially the Uranium Technical Sub-Committee dealt with the production of pyrite and sulphuric acid required by the uranium industry, but in view of the magnitude of this undertaking it was decided in December 1952 to establish an Acid Distribution Committee to undertake this function.

There was, of course, virtually no sulphuric acid available in South Africa for the uranium industry and it was necessary to install acid plants for this purpose. With the exception of a 40 ton per day auto-oxidation plant at Stilfontein, contact acid plants have been installed to meet the requirements of 1300 tons per day as follows:

Mine	*Daily capacity, tons H_2SO_4*	*Date started or to be started*
West Rand Cons. Mines, Ltd.	50	Sept. 1952
Daggafontein Mines, Ltd.	220	March 1953
Western Reefs Expl. and Dev. Co. Ltd.	220	Sept. 1953
Randfontein Estates G.M. Co. W. Ltd.	220	Feb. 1954
Stilfontein G.M. Co. Ltd.	40	Dec. 1954
Virginia O.F.S. G.M. Co. Ltd.	330	Jan. 1955
Stilfontein G.M. Co. Ltd.	150	Oct. 1955
Blyvooruitzicht G.M. Co. Ltd.	150	May 1956
TOTAL	1380	

A capacity of 1380 tons per day with a requirement of 1300 tons per day allows a desirable spare capacity of about 6%.

All of the sulphuric acid in the uranium industry is being or is to be made from iron pyrite which is fortunately available in the uranium plant residual pulp in several mines in sufficient quantity to justify its recovery and, for this purpose, flotation plants have been or are to be installed at mines:

In addition to the 650 tons FeS_2 per day which will be recovered from flotation plants within the uranium industry, 35 tons per day will be obtained from the West Rand Consolidated Mines, Limited, where pyrite has been recovered for many years by gravity concentration and sold to the African Explosives Company for the manufacture of sulphuric acid for use in explosives and fertilizer.

Mine	*Estimated production, daily tons FeS_2*	*Date started or to be started*
Daggafontein Mines, Ltd.	155	April 1953
Western Reefs Expl. and Dev. Co., Ltd.	155	Sept. 1953
Vogelstruisbult G.M. Areas Ltd.	90	Dec. 1954
Virginia O.F.S. G.M. Co. Ltd.	180	July 1955
Harmony G.M. Co., Ltd.	70	May 1956
TOTAL	650	

However, to manufacture 1300 tons of acid per day requires 885 tons of FeS_2 per day so that there is an apparent shortfall of 200 tons of FeS_2 per day and it is hoped that this will be available from the Government Gold Mining Areas (M) Consolidated, Ltd., where there is a pyrite recovery flotation plant dealing with cyanided residual slime. Portion of the capital for this was financed by loan from the Combined Development Agency.

The production and distribution of pyrite and acid required in the uranium industry is controlled by the Acid Distribution Committee, which recommends when and where pyrite and acid plants should be installed. Guiding principles in this connection are to locate these plants at such points as will ensure a minimum price of acid delivered to uranium plants. At the present time, because Virginia O.F.S. G.M. Company, Limited and Harmony G. M. Company Limited, have not yet started pyrite production, the Committee has been obliged to purchase pyrite from outside sources, even to the extent of importing pyrite from overseas, but it is hoped that this will be only a temporary measure.

The capital costs of the combined acid plants used in the industry are about £7,000,000 and the combined costs of flotation plants (excluding Govenrment Areas plant), used primarily for the production of pyrite, are about £2,000,000.

To meet the limestone and lime requirements, local factories have extended their productive plants. This applies also to glue, nitric acid and ammonia.

The manganese ore is obtained from nearby local deposits but it was because of the limited available supply from this source that provision was made in virtually all of the uranium plants for the recovery of manganese dioxide from effluent solutions from these plants.

Electric power for the Gold Mining Industry is obtained from the Electricity Supply Commission and to facilitate an increase in the production of power to meet the requirements of the uranium industry, money was loaned by the Combined Development Agency to the Electricity Supply Commission.

The uranium project has necessitated the training and employment of about two thousand white employees and about 4000 native employees and a large building scheme had to be inaugurated to house these employees. The acid and pyrite plants also had to be staffed and operated and, in connection with the acid plants, African Explosives and Chemical Industries, Limited, rendered valuable assistance.

It may be of interest to note that the contact acid plants used in this uranium industry were the first in the world to use fluo-solid roasters.

The Uranium Technical Sub-Committee was also responsible for the design and installation of the central works at Calcined Products (Pty.) Limited, where the wet final product from all uranium producers is dried, calcined, sampled and packed for shipment overseas.

Although there are now many uranium plants in successful operation, the process is by no means perfect and there is still ample scope for research. This continues to be done in the laboratories of the producers, at the Governmental Metallurgical Laboratory, at Calcined Products (Pty.) Limited, and both in the United States of America and in the United Kingdom.

From what has been written, it is obvious that the launching of the uranium industry in South Africa has placed a considerable strain on the economic resources of the country. On the other hand, it has created new employment for metallurgists, chemists and a host of others and undoubtedly will increase the country's economic strength.

THE SOUTH AFRICAN ATOMIC ENERGY BOARD

The Atomic Energy Board was brought into being in 1949 and it was the Board which made the agreement with the overseas Combined Development Agency for the sale and purchase of the South African uranium output until about 1965. The Gold Mining Industry is represented on the Board.

The Board appointed an implementing committee called the Uranium Production Committee which concerns itself with all matters pertaining to the industry and, amongst other things, it examines critically all applications from companies to become uranium producers and recommends to the Board as it thinks fit. The Government Mining Engineer is the Chairman and the Industry is represented on this Committee.

The Board also appointed a Health Hazard Committee to ensure satisfactory working conditions for the employees on uranium plants. It also appointed a Security Committee to report on all matters affecting security, secrecy, etc.

THE FUTURE OF THE SOUTH AFRICAN URANIUM INDUSTRY

At the present time South Africa produces uranium oxide only and it has not embarked as yet on the further processing of the oxide. The disposal of its output is assured until about 1965 and what happens thereafter will depend upon what developments take place in the application of nuclear energy between now and then, and upon other discoveries of uranium ore which may be made elsewhere. South Africa is fortunate that the cost of mining and milling uranium ore is usually debited against gold production and therefore, on this basis, it may prove economic to continue to recover uranium from these relatively low grade ores for many years beyond 1965. It is certain that the recovery of gold from these ores will continue for very many years and so it would not appear unrealistic to believe that uranium will continue to be produced in South Africa for many years also.

ACKNOWLEDGEMENTS

Much of the contents of this paper appeared in an address by C. S. McLean entitled "The Uranium Industry in South Africa" which was presented to the Chemical, Metallurgical and Mining Society of South Africa, and was published in April, 1954, in the proceedings of that Society. Due acknowledgement is made, therefore, to the Chemical, Metallurgical and Mining Society for permission to draw so freely upon its proceedings for this paper.

Extraction of Uranium from Low Grade Uranium Ores*

By Bela Bunji,† Yugoslavia

Ore bodies of uraninite and uranothorianite of South Yugoslavia are especially interesting with regard to the extent of their occurrence. The configuration of the occurrence offers vast possibilities for an intensive exploitation from a mining point of view.

Uranium occurs as uraninite and uranothorianite disseminated in granite mass. The particle size of these radioactive minerals varies from 10 microns to 2000–3000 microns, but the major part is under 30 microns.

Exploration has shown a large ore deposit assaying 40–120 gm uranium/ton of ore.

The percentages of the granite material assays as follows: SiO_2, 65.80; Al_2O_3, 14.48; Fe_2O_3, 3.21; CaO, 2.68; MgO, 1.64; K_2O, 2.8; Na_2O, 4.17; FeO, 1.02; S, 0.47; H_2O, 0.48.

This investigation is concerned with the technology of extracting uranium from the ore and recovering it in the form of a uranium oxide concentrate.

From many preliminary tests, the most favorable results were obtained by pressure leaching with sodium carbonate–sodium bicarbonate solutions.

Special attention was paid to the following problems: (*a*) getting uranium into solution, (*b*) concentration of uranium in solution, and (*c*) economy of these two processes.

LEACHING TESTS

Leaching tests were carried out in a normal steel vessel of 200-liter capacity. The contents were agitated with air-lift pumps. The vessel was heated by passing steam through an external part of the vessel. Oxygen was supplied in the form of air with a compressor. A sampling tube permitted samples to be taken during test.

PARTICLE SIZE

It has been stated that the recovery of uranium increases with the fineness of grind. A grind of −150 mog has given optimum results. Increase of particle size decreases recovery. By 65 mog, the recovery was 40–50 per cent and there was no possibility of increasing this by alteration of other conditions, but by grinding recovery increased and reached its maximum at −150 mog. Furthermore this maximum was not exceeded by finer grinding.

The necessity of very fine grind indicated a homogeneous disposition of uranium in the material, so that its solubility was proportional to the surface of ore.

CONCENTRATION OF Na_2CO_3

Using Na_2CO_3 solutions of different concentrations, it was shown that a 4–5 per cent solution was the most convenient. Increasing the concentration results in neither increase of dissolution nor in recovery but in fairly high solubility of silicates and other materials.

PRESSURE

Pressure favours oxidation and further dissolving. Maximum solubility was obtained at an air pressure of 3 atm. Greater recovery of uranium was not obtained by increasing air pressure, but higher air pressure increased the solubility of SiO_2. At atmospheric pressure, without aeration, 20 per cent of the uranium was obtained by the leaching of ore (see Fig. 1).

TEMPERATURE

Dissolution increases with temperature, becoming significant only at 60°C. Satisfactory results were obtained at 95–100°C. A higher temperature could not be used because of rapid solubility of SiO_2 (Fig. 2).

PULP DENSITY

Up to a certain limit pulp density did not influence the leaching. Ratios 1:6, 1:5, 1:4, 1:2 and 1:1 (solid–liquid) were used, but showed no difference in results.

LEACHING TIME

High values were obtained in the first two hours and increased very slowly thereafter, so that after two hours leaching could usually be discontinued. It should be noted that it was necessary in certain cases (depending on the concentration of uranium in the ore) to extend the leaching time to four hours.

REAGENT CONSUMPTION

Under optimum conditions for the dissolution of uranium, 12 per cent of the Na_2CO_3 is converted to $NaHCO_3$ as a result of secondary reactions. The content after reaction is 90% Na_2CO_3 and 10% $NaHCO_3$. The $NaHCO_3$ can be converted to Na_2CO_3 again with NaOH. In order to convert this 10% of

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* Paper P/965 consists of two parts. Part II follows immediately after this section.

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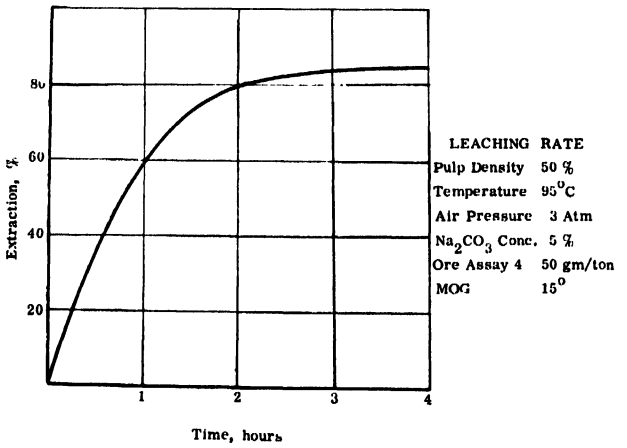

Figure 1

$NaHCO_3$ to Na_2CO_3 and thus regenerate the solution, 7.2 kg of NaOH were added per ton of ore. At the same time 50–60 gm uranium were leached per ton of ore, representing a recovery of 80–85%.

Among many tests conducted in the course of this investigation, one gave the following results:

The test was carried out in a domestically made Pachuca type autoclave of 20-liter volume. Air forced through the solution by a compressor gave the required pressure, agitation and oxidizing conditions.

Conditions of testing were: 4.5 kg of ore was ground to 80 per cent —200 mesh, 13.5 l of Na_2CO_3 5% solution, pulp density 1:3 (solids-liquid), 95°C, 3 atm pressure by aeration of 10 l air per min. Required time of leaching was 2–4 hours.

At the time of leaching, air was saturated with one liter water. The balance of 12.5 l gave the following analysis on samples of 100 ml: 2×10^{-3} gm U per 100 ml; 2.1×10^{-3} gm U per 100 ml; and 1.9×10^{-3} gm U per 100 ml. Average value of these three results gave a recovery of 55 gm of uranium per ton of ore.

By analysis of sodium carbonate and sodium bicarbonate, the following value was obtained: 44.5 gm Na_2CO_3 per 1000 ml; 4.5 gm Na_2HCO_3 per 1000 ml.

RESULTS OBTAINED BY RECYCLING OF Na_2CO_3 SOLUTION

With regard to the poor concentration of uranium in ore, and the necessary moderate concentration of Na_2CO_3 in the leach solution, it was considered necessary to re-cycle the same solution for a new leaching period. This is necessary also for later precipitation of uranium from solution.

PRECIPITATION OF URANIUM

Taking into consideration all factors influencing the choice of pulp density (consumption of energy, filtration, washing, etc.) 50 per cent solids in pulp might be considered as the most convenient density for leaching. Consequently, after a fairly long leaching, we have had 4–6 $\times 10^{-2}$ gm U/liter of solution.

By re-cycling the mother liquor, it can be concentrated with uranium. Whether we should have more re-cycling of mother liquor depends on filtration losses.

We ascertained that with a vacuum-filter, with one washing, re-pulping and re-filtration, we realized 98–99 per cent recovery from pregnant solution and in this way we did not compromise the balance of water. Losses of water occurred to air which was used for agitation and oxidation, secondly in the filter-cake, and finally as the amount of water which is sent to precipitation as a pregnant solution. This water, which escapes from the process, is re-cycled by washing, by filtration, either in the form of pure water or in the form of barren solution after precipitation. A filter capacity of 30 lb/ft²/hr is obtained by filtration of pulp containing 50 per cent solids. The screen analysis of solids is as follows: +150, 2.2%; +200, 5.55%; +270, 6.95%; +325, 18.35%; and —325, 66.95%.

The concentration of uranium in solution depends on the number of re-cyclings of mother liquor and averages from 5×10^{-2} gm/l to $5n \times 10^{-2}$ gm/l of uranium.

We ascertained that uranium can be precipitated from a pregnant solution by reduction with H_2 under pressure and in the presence of Ni as catalyst with a uranium recovery of 98–99 per cent, the barren solution containing 5×10^{-5} to 5×10^{-6} gm U/l.

During reduction, a small change in the ratio Na_2CO_3: $NaHCO_3$, from 3.8 before reduction to 4.2 after reduction was noted.

The concentration of sodium sulphate even after 10 re-cyclings of mother liquor was of the order of 10–20 gm/l.

Reduction was conducted at a partial pressure of H_2 of 9 atm and at 120°C.

A small problem was encountered in the separation of Ni from the precipitated oxide. It seemed more convenient to use nickel-gauze rather than nickel powder and we could not obtain absolute separation of Ni from the oxide, but the use of nickel-gauze is

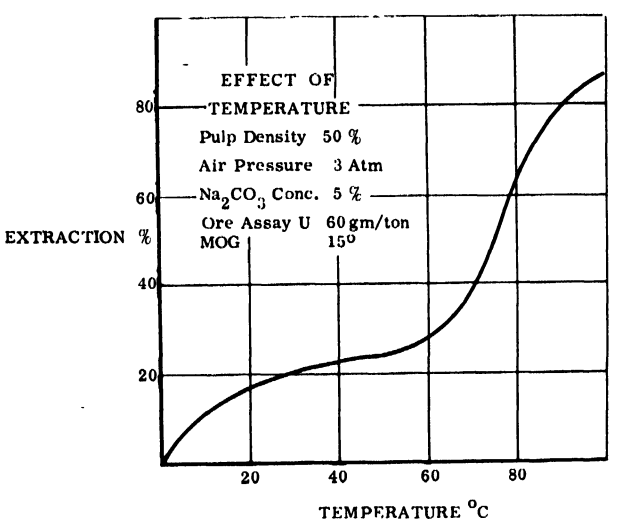

Figure 2

less effective than powder inasmuch as the active surface of the catalyst is smaller.

All experiments carried out in order to determine the technology of extraction of uranium from low grade uranium-bearing deposits of South Yugoslavia, assaying an average of from 0.004–0.012 per cent uranium have shown that it is possible to realize a recovery of 80/90 per cent of uranium by leaching under pressure.

Favorable conditions of ore-dressing to obtain a recovery of 80/90% of the uranium (depending on the uranium content of the ore) are as follows: (*a*) fineness of grind of 150 mog; (*b*) pulp density 40–60 per cent of solids; (*c*) partial pressure of oxygen 0.4–0.6 atm; (*d*) temperature of leaching 85 to 95°C; (*e*) leaching time 90–120 min; (*f*) consumption of Na_2CO_3 9 kg per ton of ore; (*g*) concentration of uranium required for precipitation obtained by re-cycling (soluble material separated from tailings with an efficiency of 98–99% in case of rich solutions. In this process the amount of solution used for washing maintained the water balance without any further operations. The filter capacity was 30 lb/ft² per hour.); (*h*) precipitation of uranium from pregnant solution by reduction under H_2 partial pressure of 9 atm by nickel as catalyst at 120°C with recovery of 98–99 per cent of uranium.

The precipitated uranium has a high purity, containing from 50–70 per cent of U_3O_8.

These deposits have the following advantages with regard to local conditions: (1) short distance from existing coal mines and energy supplies; (2) convenience of deposits for available mining exploitation on large scale of open-pit-mining; very convenient ratio between ore and overburden; (3) short distance (about 600 metres on the average) of ore-haulage to the ore-dressing plant; (4) favorable technological method of ore dressing; (5) water supplies within very short distance; and (6) convenient tailing disposal.

The construction of a continuous pilot plant, with a capacity of 40–50 tons of ore per day, is about to be completed on the basis of the results from semi-pilot-batch-testing plant.

EXTRACTION OF URANIUM FROM ASHES OF URANIUM-BEARING COALS

Coals from our different deposits contain small amounts of uranium. After burning of uranium-bearing coals, the ashes have a content of 0.05–0.015 per cent uranium.

Laboratory tests showed that sodium carbonate-sodium bicarbonate pressure leaching permits a recovery of about 85–93 per cent.

Testing was carried out in an autoclave and vessels of stainless steel of 5-liter volume. A mechanical mixer agitated the pulp, and made possible by high speed a continuous intimate contact of the pulp with oxygen.

Optimum results were obtained under the following conditions: (*a*) fineness of grind 100 mog; (*b*) pulp density 40–60 per cent of solid; (*c*) oxygen pressure 12 atm; (*d*) temperature 130–150°C; (*e*) leaching time 4 hours; and (*f*) concentration of Na_2CO_3 15–20 per cent.

With regard to the possibility of concentration of using these coals in 2–3 places in the country, present results of the technology of uranium extraction show a real possibility of uranium production from these raw materials.

The Extraction of Uranium from Sconza Shales

By Vladimir G. Logomerac,* Yugoslavia

This is a report of work which was done in the last few years, with the aim of extracting uranium from low grade ores.

The ore was a Sconza shale from Idrija, a kind of bituminous shale, containing more than 1 per cent of mercury. A rich deposit of this ore existed and the mercury had been produced from it for the last 400 years. The uranium content was on the average 136 grams per ton, while the typical analysis of ore (in per cent) was the following: SiO_2, 69.12; Al_2O_3, 15.91; Fe_2O_3, 3.61; CaO, 1.40; MgO, 1.38; P_2O_5, 1.44; S, 1.95; and C, 5.55.

The presence of a considerable amount of organic materials, as well as mercury and vanadium was significant for the methods which could be used for the solution of the extraction problem, especially as it was necessary to assure later the normal production of mercury from the leached ore.

A further difficulty was presented by the fact that the uranium occurs in such a form that it cannot be concentrated by gravity or flotation methods, so that the only method left was the extraction metallurgy, i.e., treatment of ores by different chemical processes. It should be mentioned that we obtained a certain degree of concentration of low grade ore by gravity methods, but the cost was high and the concentration was incomplete and inefficient.

The work on this problem was done in three different directions: (1) acid treatment of ore-leaching with sulphuric and nitric acid; (2) carbonate treatment of ore-alkaline leaching with sodium carbonate; (3) chlorination of ore. Work was done first on laboratory scale, and later in a pilot plant with a capacity of about 3 tons of ore daily. We made a systematic study of the influence on the extraction of such factors as the time and temperature of leaching, the ratio ore/solution, the concentration of acid and sodium carbonate in the solution, the optimal ore grains diameter and so on.

The leaching of ore, and also the treatment of the solution in the pilot plant, was made in a reaction apparatus where very effective stirring of pulp was obtained by a special pump. The separation of precipitate and ore was made by centrifugals, while the extraction of uranyl nitrate solution was made by a "Luwesta-Solvent extractor." The precipitation of uranium from the solution obtained by the extraction, was done by H_2O_2, or NaOH, or NH_3 in the usual manner.[1,2,3]

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The aim of this work was to test the processes which were developed in the preliminary investigations on the laboratory scale. We also wanted to obtain data of practical value for the leaching of ore and the precipitation processes. Finally, it was necessary to find the exact consumption of material and chemicals, and the percentage extraction of uranium from the ore.

It was found that other kinds of ores also can be treated in the same pilot plant with the same success. We tried different kinds of leaching, with many different ways of treating the resulting solution, to find their practical value in relation to the percentage extraction and the cost of the production.

EXPERIMENTAL

We shall now describe the work done with the shale, the analysis of which was given before, and which had grinding characteristics as follows:

DIN	*Diameter*	*Per cent*
4	1.50 mm	13.90
8	0.75 mm	34.36
11	0.54 mm	5.73
50	0.12 mm	28.82
60	0.102 mm	1.49
80		1.42
100	0.06 mm	1.80
— 100	— 0.06	12.50

As we see, 53.99% of grains have a diameter greater than 0.54 mm. This influenced the extraction rate of uranium from the ore since it was found that with an increase of the grain fineness to 17.86% greater than 0.54 mm the percentage of uranium extraction is increased by 5–10%.

The uranium was extracted from the ore by processes commonly used today: carbonate leaching gave about 60% efficiency (without autoclave), while leaching with sulphuric acid gave 75–80%, and with nitric acid about 90%. Re-cycling of solutions was carried out so that the consumption of chemicals was small. The use of catalysers in the leaching process did not show any significant improvement of the uranium extraction.

The procedure was to charge a given amount of ore (250–500 kg) in a solution of desired composition, with a definite ratio ore/solution. The optimum value of this ratio was 1/1.7 for the work with acid, and 1/3 for the alkaline process. During the process the pulp was vigorously stirred at a definite temperature and when working with alkaline solutions air was blown through. Samples of the ore and the solu-

tion were taken periodically and analyzed to determine the leaching rate, uranium extraction and reagent consumption. Uranium was determined by colorimetric method[4] or fluorimetrically.[5]

Several months of work on this pilot plant have shown that the work with acids has more advantages. The optimum working conditions are the following:

Ore/solution ratio	1/1.7 and 1/3	
Temperature	80°C	95°C
Time of leaching	1 hour	1 hour

and the chemical consumption per ton of ore was as follows: sulphuric acid, 50 kg; nitric acid, 45 kg; sodium carbonate, 50 kg.

With nitric acid solution one can proceed directly to the extraction while the sulphuric acid and carbonate solution have to be treated by various methods in order to obtain a precipitate with the highest possible concentration of uranium which is then dissolved in nitric acid and sent for extraction.

Among the different procedures and processes which were developed, we shall describe here the following: (1) precipitation of uranium from solutions by ammonium sulphide solution; and (2) direct extraction of uranium from solution with a low concentration of uranium.

PRECIPITATION OF URANIUM FROM SOLUTIONS BY AMMONIUM SULPHIDE

The process for dissolving the uranium compounds in sulphuric acid or Na_2CO_3 is well known, and will not be described here.[6,7] The solutions obtained by leaching of ore with H_2SO_4 or Na_2CO_3 were then treated according to the following scheme.

H_2SO_4 — solution
↓
CaO up to pH of 3.5–4 (1)
↓
The precipitate, after washing with 10% H_2SO_4 is rejected
NaOH or NH_4OH up to pH 5.6–5.8
↓
$(NH_4)_2S$
↓
Filtrate rejected
Uranyl sulphite

Na_2CO_3 — solution
↓
H_2SO_4 up to pH 10
↓
Solution with complex uranyl carbonate
Precipitate rejected
↓
H_2SO_4 up to pH 4
↓
Boiled to expel the CO_2 (2)
↓
NaOH up to pH 5.6–5.8
↓
$(NH_4)_2S$
↓
Uranyl sulphide
Filtrate rejected

As can be seen from the preceding scheme, the process was carried out with acid as well as alkaline solution. The procedure showed itself to be very rapid and convenient for large scale work.

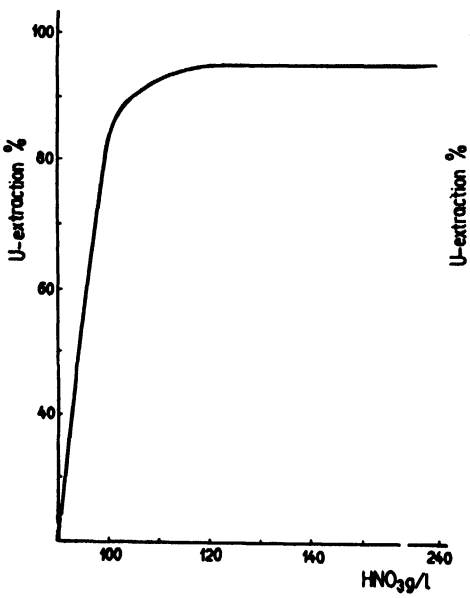

Figure 1B.
Effect of HNO_3 on U-extraction

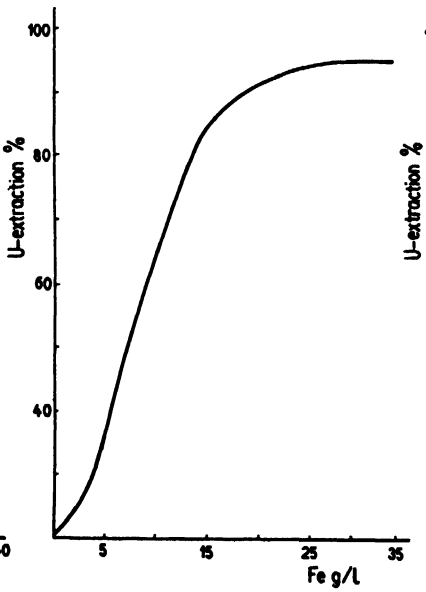

Figure 2B.
Effect of Fe on U-extraction

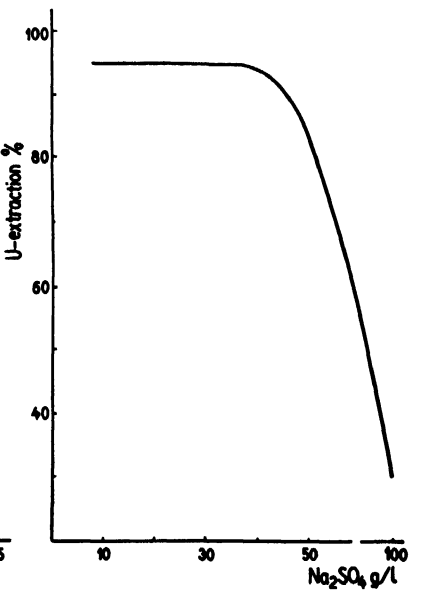

Figure 3B.
Effect of Na_2SO_4 on U-extraction

The initial solution had in both cases a pH of 3.5–4. In the first case this was obtained by adding lime to the solution to bind the excess acid. The resulting precipitate of $CaSO_4$ and other hydroxides was then centrifuged and, as it contains some trapped uranium, it was washed with 10% H_2SO_4. After that the residue was rejected while the sulphuric acid solution with uranium was used for the new charge.

In the second scheme, the sulphuric acid solution was treated with sodium carbonate up to a pH of 10, so that the uranium went into the solution. This solution was then brought to pH of 3.5–4, by adding sulphuric acid, after which the CO_2 was expelled by boiling. As is well known, carbonates form complex uranyl compounds and prevent the precipitation of uranyl sulphide.

We had not time to investigate the possibility that the destruction of carbonate may be avoided by boiling and by direct precipitation of acid solution with $(NH_4)_2S$, so that the H_2S formed drives out the CO_2 from the solution.

It is known that uranyl sulphide precipitate with $(NH_4)_2S$ from alkaline solutions, gives a dark-brown substance.[8] Because of that, the solution which was obtained was brought to pH of 5.6–5.8 by addition of ammonia or better of NaOH, after which the precipitation with $(NH_4)_2S$ was carried out according to the reaction:

$$UO_2^{++} + HS^- + NH_3 \rightarrow UO_2S + NH_4^+$$

The precipitation of uranyl sulphide can be made in the whole range of temperature between 20–80°C. The addition of $(NH_4)_2S$ solution was continued until the precipitation of sulphide stops, which is usually attained at pH of 8–9. The whole precipitation process, from the moment when pH of 4 is reached up to the end, lasts about 10–20 minutes. The precipitation of uranium is quantitative, especially if one adds 0.5 kg iron hydroxide as carrier per ton of ore. The consumption of reagents, time of process and yield of U extraction were as follows:

	Reagents (per ton of ore)	*Time of process*	*Yield*
1.	(50 kg H_2SO_4)	1 hr at 70–80°C	75–80% U
	25 kg CaO	30 min at 40°C	80–90% U
	38 kg NaOH		
	30 l $(NH_4)_2S$	10–20 min at 40°C	100% U
2a.	(50 kg H_2SO_4)	1 hr at 70–80°C	75–80% U
	(90 kg Na_2CO_3)	1 hr at 60°C	80–90% U
	15 kg H_2SO_4		
	and boiling	1 hr at 95°C	
	5 l $(NH_4)_2S$	10 min at 30–40°C	100% U
2b.	(50 kg Na_2CO_3)	1 hr at 95°C	60% U
	(20 kg H_2SO_4)		
	and boiling	1 hr at 95°C	
	c l $(NH_4)_2S$	10 min at 30–40°C	100% U

DIRECT EXTRACTION OF URANIUM FROM SOLUTION WITH LOW URANIUM CONTENT

As the majority of our ores contains 100–500 gm uranium per ton, we paid special attention to the processes for the direct extraction of uranium from the solution resulting from leaching of such ores.

The work was done with the same ore used previously, but the grinding was better, as can be seen from the following grinding analysis:

DIN	*Diameter*	*Per cent*
4	1.50 mm	1.32
8	0.75 mm	9.14
11	0.54 mm	7.40
50	0.12 mm	52.94
60	0.102 mm	2.66
80		5.50
100	0.06 mm	0.90
— 100	— 0.06	19.80

The charge was 250 kg, the ratio ore/solution was again 1/1.7, the temperature of leaching was between 70-80°C, with constant stirring for 30–60 minutes. The reaction of leaching, with nitric acid, was finished within the first 30 minutes.

The leaching of ore with different concentrations of nitric acid gave the following results:

%HNO_3	*Per cent U*
2	50–60
4	65–75
6	70–80
8	85–95

The resulting solution was examined especially with regard to the content of $SO_4^=$ and, if it was more than 50 gm per liter of solution, it was blocked or precipitated with the addition of lime. The resulting precipitate was centrifuged, washed and rejected. The filtrate was examined on the content of HNO_3, Fe^{++}, Ca^{++} and $SO_4^=$ and if necessary corrected to the optimum content of these materials and then sent to the ether extraction.

Extraction was made with "Luwesta-Solvent extractor", type 2006, made by Westphalia Separator A.G., Oede, Westfallen. This apparatus works continuously on the countercurrent principle with three stages of extraction. The apparatus can also separate solid substances brought in with the initial solution or formed in extraction, which is very convenient.

The extraction of nitrate solution, the specific gravity of which was between 1.15–1.4, was made with technical ether of specific gravity 0.73. The influence of HNO_3, Fe^{++}, Ca^{++} and $SO_4^=$ concentration on the efficiency of the uranium extraction was investigated several times.

The influence of pressure of mixing during the extraction and also the ratio of both solutions on the uranium extraction were investigated. The results of these investigations are shown in the table below.

From the data given above, we can come to the following conclusions:

1. The influence of the concentration of the nitrate solutions, and of Fe and Na_2SO_4 are shown in Figs. 1–3. The diagrams show that Fe^{++} together with the other components of solution have a great influence on the efficiency of Uran extraction. From our experience the optimum composition of the solution for the extraction would be the following (in gm/l): HNO_3, 110–130; Fe^{++}, 18–22; Ca^{++}, 10–20; Na_2SO_4, 0–40.

2. The optimum pressure of nitric solution during the extraction is 1.5 atm. An increase to 1.75 atm has no effect, while a decrease to 1.25 atm decreases the effect of uranium extraction. So far as ether is concerned, the optimum extraction is obtained when the ether is mixed with nitrate solution without pressure. The increase of pressure does not seem to have any effect on the extraction, except that it increases the consumption of ether.

3. We have also investigated the ratio of nitrate solution to ether, for the following values

300 : 500 (1:1.67)
300 : 300 (1:1)
500 : 500 (1:1)
500 : 300 (1.67:1)
500 : 200 (2.50:1)

from which values we can see that the volume of nitrate solution can be 1.67 up to 2 times greater than the volume of ether.

CONCLUSION

An attempt has been made in this paper to examine the problems of leaching bituminous shales with uranium content of average 136 gm per ton of ore and to describe the data of leaching, precipitation scheme and techniques, as well as the extraction.

Two effective procedures have been described. The precipitation of the solution, obtained by different methods of leaching, with $(NH_4)_2S$ seems to be very attractive and effective, and yields consistently high uranium extraction from the solution even with low uranium content.

Leaching with HNO_3 and direct extraction of nitrate solution with ether, without any precipitation between, also yield to 90–95% uranium extraction from any ore we investigated. The data for optimum nitrate solutions content are given, as well as other data of extraction.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made by the author to Professor P. Savić, who proposed the procedure and the scheme for the precipitation with ammonium sulphide. The author also wishes to thank Mr. C. M. Teofilovski and B. V. Radosavljevic for the constant collaboration and help they gave him in this work.

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	HNO_3 gm/l	Fe gm/l	Ca gm/l	Na_2SO_4 gm/l	Uran gm/l	Solution l	:	Ether l	Solution atm	:	Ether atm	Uran extraction, %
1.	159.7			18.81	0.07	300	:	500	1.5	:	0	63.8
2.	159.7			18.81	0.07	300	:	500	1.25	:	0	37.0
3.	120.1	3.94	21.90	51.20	0.124	300	:	300	1.5	:	0	30.0
4.	120.1	3.94	21.90	51.20	0.124	500	:	500	1.5	:	0.25	30.0
5.	120.1	3.94	21.90	51.20	0.124	500	:	300	1.5	:	0.25	30.0
6.	120.1	3.94	21.90	51.20	0.124	500	:	300	1.75	:	0	30.0
7.	243.0	22.66	7.7	25.00	0.150	300	:	300	1.75	:	0	65.8
8.	243.0	22.66	7.7	25.00	0.150	300	:	300	1.5	:	0	88.2
9.	243.0	22.66	7.7	25.00	0.150	500	:	500	1.5	:	0	88.9
10.	108.6	17.94	1.30	26.89	0.181	500	:	300	1.5	:	0	29.6
11.	128.4	18.82	1.26	113.80	0.181	500	:	300	1.5	:	0	29.6
12.	110.0	27.24	0	101.00	0.216	500	:	300	1.5	:	0	29.6
13.	132.3	19.70	48.6	37.84	0.081	500	:	300	1.5	:	0	93.8
14.	102.0	15.0			0.094	500	:	300	1.5	:	0	87.1
15.	102.0	15.0			0.094	500	:	200	1.5	:	0	82.4
16.	139.0	16.62		29.74	0.083	500	:	300	1.5	:	0	86.9
17.	139.0	16.62		29.74	0.083	500	:	200	1.5	:	0	85.5
18.	139.0	16.62		29.74	0.083	500	:	200	1.75	:	0	83.9
19.	114.0	17.24	32.07	32.07	0.165	500	:	300	1.5	:	0	95.8
20.	115.0	15.92	24.63	24.63	0.175	500	:	300	1.5	:	0	95.4
21.	116.6	17.24	14.85	16.90	0.190	500	:	300	1.5	:	0	92.0
22.	111.4	17.35	11.04	21.40	0.175	500	:	300	1.5	:	0	87.5
23.	102.8	17.68	11.04	25.54	0.168	500	:	300	1.5	:	0	95.3
24	124.0	39.02	5.03	42.79	0.190	500	:	300	1.5	:	0	94.6
25	130.0	19.35	19.74	14.52	0.213	500	:	300	1.5	:	0	96.6
26.	126.0	22.22	13.19	24.04	0.255	500	:	300	1.5	:	0	91.0
27.	121.9	22.88	13.9	23.9	0.262	500	:	300	1.5	:	0	91.2
28.	110.6	20.78	14.62	18.06	0.262	500	:	300	1.5	:	0	97.0
29.	110.6	20.78	14.62	18.06	0.262	500	:	300	1.5	:	0	94.7
30.	126.0	19.35	19.14	14.25	0.147	500	:	300	1.5	:	0	94.9
31.	128.6	23.44	16.94		0.263	500	:	300	1.5	:	0	94.1

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Chemical Aspects of the Uraniferous Zirconium Ore of Poços de Caldas (Brazil)

By F. J. Maffei, João R. Pucci and W. Ferreira,* Brazil

For a long time it has been known that the zirconium ore found in large quantities in the Brazilian plateau of Poços de Caldas shows a marked radioactivity but only recently has it been connected with its uranium content. Some samples of the ore run as high as 2% U_3O_8; very few samples have been found with less than 0.2% and the general average is of the order 0.5 to 0.6% U_3O_8. Under the auspices of the Brazilian Research Council a systematic study of the chemical behavior of the mineral has been undertaken to determine conditions for the separation of uranium. This paper presents an account of the results obtained, with analysis of the ore, and the effect of many chemicals on the solubilization of the uranium and other components of the ore.

INTRODUCTION

The Brazilian Plateau of Poços de Caldas has been for a long time known for the occurrence of large beds of zirconium minerals variously named in the literature as "caldasite", "baddeleyite", "brazilite", "zirkite", "zirkelite", and "favas". Commercial lots, with a ZrO_2 content ranging from 70% up to 85% have in the past been exported from Brazil. Individual samples with more than 90% ZrO_2 are frequently found.

Venable[1] gives a fair brief account of the deposits of Poços de Caldas in the following words:

> "The deposits are in the Caldas region which lies partly in the State of Minas Gerais and partly in the State of São Paulo, approximately 130 miles north of the city of São Paulo. It is a mountainous plateau, the main elevation of which is about 3600 feet. The surface is undulating, presenting differences in level of from 300 to 600 feet. The whole area is bounded on all sides by ridges rising abruptly from 600 to 1200 feet above the general level and forming a roughly elliptical inclosure with a major axis of approximately 20 miles in length and a minor axis of 15 miles. The predominant rock of the plateau is phonolite.
>
> "The ore can be divided roughly into two classes. First, alluvial pebbles ranging in size from one-half inch to three inches in diameter, generally carrying about 90–93 per cent of zirconia. The pebbles, known as "favas" and having a density of 4.8–5.2, are found along small stream beds and on the talus slopes of low ridges. Second, zirconia ore proper or zirkite, which ranges in shade from a light gray to a blue-black, the lighter colored material carrying a larger percentage of zirconium silicates and showing a minimum content of 73 per cent zirconia. The blue-black ore generally carries 80-85 per cent of zirconia."

The ore is a mixture of oxide and silicate, its ZrO_2 content seldom being lower than the theoretical content of the silicate. As impurities, ferric oxide and sometimes titanium oxide are the major impurities; aluminium and uranium range from a few tenths to around 2%. Of the minor impurities, phosphorus and manganese are found as a few tenths of one per cent and of course hafnium is always present.

The zirconium ore of Poços de Caldas has been known to be radioactive for a long time, but its relation to the significant amount of uranium present in the ore has only recently been established.

Hevesy[2] states that all zircons exhibit radioactivity by virtue of presence of minute amounts of uranium and thorium and that the radioactivity of zircons show a rough parallelism with their hafnium content. Lee[3] recognizes that, if a zircon is found markedly radioactive, it is reasonably certain that the mineral will prove to contain an appreciable amount of hafnium. It is unfortunate that his list of hafnium-bearing zirconium minerals does not show any data relating to the radioactivity of the minerals analysed.

Our work confirms in broad lines the above statement although we have not been able to determine the hafnium content with a great precision but all the zirconium minerals of Poços de Caldas show the presence of hafnium and owe their radioactivity to the uranium content. This rule has been confirmed by a high hafnium (around 10% Hf) zirconium mineral from the northwest part of Brazil with an uranium content of above 4%.

So far we have not been able to detect any appreciable amount of thorium associated with zirconium ore that we have tested so its radioactivity is a direct measure of its uranium content.

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It is quite interesting to note that in the same plateau of Poços de Caldas is found a hill formed chiefly of iron ore which shows a very marked radioactivity; the uranium content is very low in contrast to a high thorium content as shown in Table I.

Table I. Uranium and Thorium Content of an Iron Ore of the Plateau of Poços de Caldas

Radiometric equivalent in % U_3O_8	*% U_3O_8*	*% rare earths*	*% ThO_2*
0.32	0.05	3.6	1.44
0.50	0.04	11.9	1.59
0.62	0.01	12.0	2.36

A representative analysis of the zirconium ore of Poços de Caldas, resulting from a sample collected from more than one hundred commercial shipments, is shown in Table II.

Table II. Average Analysis of Commercial Zirconium Ore of Poços de Caldas

Loss on ignition (1000°C)	2.9 %
SiO_2	14.1 %
MnO	0.38%
Fe_2O_3	6.1 %
TiO_2	1.2 %
Al_2O_3	2.3 %
P_2O_5	0.26%
ZrO_2	75.6 %
U_3O_8	0.6 %

No connection between the major constituent and uranium content can be found. Table III shows samples which exemplify this statement.

ANALYTICAL PROCEDURES

Before going further in this report it is proper to state briefly the analytical procedures followed in this work. As it is known, zirconium minerals are very refractory to chemical attack, and the silicate is even more refractory than the oxide.

This has to be borne in mind when the ore has to be decomposed for its solubilization. The sample should be minus 200-mesh and as opening reagents strong fluxes such as borax, bifluorides or potassium bisulfate should be used. In this work the bisulfate has been preferred even though a few tenths of one per cent of zirconium silicate remains unattacked.

The separation of uranium has been accomplished by the use of cupferron-carbonate in many instances but the most usual procedure has been the extraction of uranium by ethyl ether.[4,5]

Table III. Uranium Content Compared with Contents of Major Constituents of Zirconium Ore

% U_3O_8	0.70	1.16	0.82	0.25	0.71	0.31
% ZrO_2	82.2	75.0	71.5	69.9	74.3	62.5
% SiO_2	5.2	12.0	24.0	26.8	23.3	19.0
% Fe_2O_3	7.9	2.9	2.7	1.9	1.8	5.6

The final uranium content has been obtained mostly by spectrophotometric means, by fluorimetric determination in case of extremely minute quantities and by weighing of uranium oxide in case of larger quantities.

As said above, the radioactivity of the zirconium ores of Poços de Caldas is due entirely to its uranium content, no thorium having been found in significative amounts. The equivalent uranium content measured with a Geiger counter is a valuable and simple way to check the results obtained in the analysis of the ores. The graph (Fig. 1) exemplifies the excellent agreement between radiometric uranium equivalent (full line) and uranium content by chemical analysis (points).

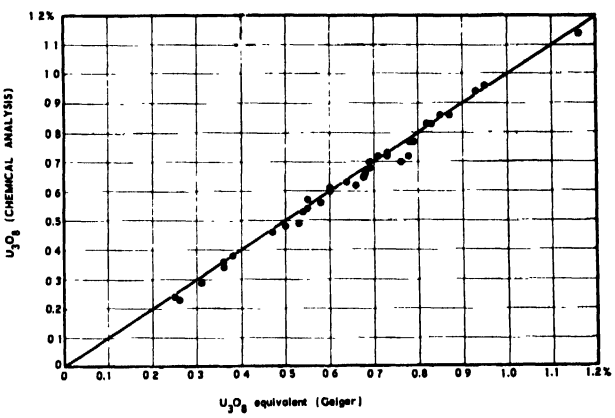

Figure 1. U_3O_8 content by chemical analysis and radiometric determination

The following results show the good checks obtained on different samples using the procedures referred to above (results in % U_3O_8).

Cupferron	*Ether extraction*	*Fluorimetric*	*Radiometric*
0.40	0.40		0.40
0.43	0.42		0.42
0.54		0.53	
0.69		0.66	
0.22		0.27	
	0.42	0.43	0.46
	0.54	0.51	0.55

Laboratory Investigations for the Industrial Separation of Uranium

The sizable quantity of uraniferous material found in Poços de Caldas and its high content of uranium were thought to justify a thorough study of the possibility of utilizing this material as a source of uranium for atomic purposes.

Petrographic studies of the minerals followed by chemical tests showed that uranium is not found as an individual mineralogical species apart from the rest of constituents of the mineral and that the uranium is either extremely dispersed or—which seems much more probable as inferred by its chemical behavior—belongs at least partially to the crystal lattice of the zirconium oxide and its separation is feasible only if the lattice is destroyed. It seems that the substitution of the uranium for

the zirconium is limited and an equilibrium between both elements in the lattice is attained when the uranium is of the order of less than one per cent. The excess content is much more amenable to extraction by relatively mild treatment with acids which do not strongly attack the ore. The results found in Table IV show that the uranium extracted by concentrated nitric acid at temperature of 150°C somewhat parallels the uranium originally present in the ore and that the extraction has no relation to the amount of ore attacked.

Table IV. Attack with Nitric Acid

% U_3O_8 in original ore	% U_3O_8 extracted	% Ore Attacked
0.38	0.05	7
0.47	0.13	10
0.50	0.10	18
0.58	0.10	14
0.63	0.14	7
0.75	0.07	20
0.80	0.03	10
0.88	0.07	7
1.15	0.38	5
1.29	0.88	6
1.39	0.80	6
1.65	1.44	13
2.00	0.75	7
2.20	1.76	10

The amount of uranium extracted shows limited dependence on the time of extraction, in one case 10% of the uranium present being extracted in 1 hour and not more than 24% in 30 hours.

When the uranium is extracted in large proportions, the concentration of the nitric acid does not affect the results significantly as is shown by the following example: extracted by 10% nitric acid, 27% of the uranium content; by 25, 50 and 70% nitric acid, 34% of the uranium content.

The results of extraction with different acids are found in Table V. Table VI shows the results with a 0.65% U_3O_8 ore in a mixture of sulfuric and hydrofluoric acids which was found particularly efficient. But here we see that the increase in uranium extracted is the result of increased attack of the ore.

Table V. Extractions with Acids

% U_3O_8 in ore	% of the U_3O_8 content recovered			
	HNO_3	H_2SO_4	HF	HCl
1.7	54	70	40	60
0.65	11	15	20	6.5

Mixtures of nitric and hydrochloric acids did not show any improvement on the extraction efficiency of either of the acids alone.

The solubility of uranium in acids is decreased if the ore is previously heated to high temperatures. A sample of 0.60% U_3O_8 ore, from which 24% of the uranium could be extracted by nitric acid, after being calcined at 1000°C, showed a solubility of 20%. Much more pronounced is the effect of heat

Table VI. Uranium Extraction with Mixtures of H_2SO_4 and HF

Parts acid in mixture for 1 part of ore			% unattacked ore	% of the original U_3O_8 content recovered
H_2SO_4	HF	H_2O		
5	1	0.5	80	26
10	1	1	60	50
10	2	1	51	54
10	2	1	43	54
10	3	1	33	75
10	3	1	33	75

on ores with higher uranium content: a 1.6% U_3O_8 ore, when heated at 1000°C gave 32% of its uranium content to nitric acid against 58% when extracted before calcining.

Results so far given refer to tests carried out with acids at temperatures as high as 150°C. With nitric acid, tests carried under pressure of 10 atm did not show any improvement over tests carried at lower temperatures.

The results reported above show also that with the average ore (0.60% U_3O_8) higher extractions of uranium are only possible if the zirconium ore is also decomposed.

With sulfuric acid at temperatures above 300°C in 3 hours the ore can be decomposed resulting in a solubilization of 90% of the uranium.

The ore remaining unattacked is mainly zirconium silicate. Excess acid can be eliminated by heating around 600°C, leaving the solubility of uranium unaffected.

High recovery of soluble uranium can be gained by fusion of the ore with common fluxes. With sodium carbonate the total decomposition of the mineral is not possible and the uranium is only partially recovered as is shown in Table VII. In tests 1 to 4 shown therein, one tenth of a part was added as sodium nitrate and in test 5 as sodium fluoride.

Table VII. Recovery of Uranium by Fusion with Sodium Carbonate

Test no.	Part Na_2CO_3 to 1 part of ore	% U_3O_8 recovered
1	0.2	34
2	0.5	39
3	1	56
4	3	72
5	1	70

Fusion with either sodium chloride or sodium fluoride showed very poor results. Fusion with a mixture of both gave only 25% solubilization of uranium.

Sodium hydroxide gave results somewhat higher. Fusion of one part of ore with one part of caustic soda, at 800°C, gave 58% solubilization of uranium. Lower or higher proportions of NaOH brought lower results.

Fusion with sodium hydroxide to which sodium nitrate was added showed slight improvement in the recovery of uranium.

Sodium hydroxide with sodium chloride or with sodium fluoride affected very favorably the recovery of soluble uranium as Tables VIII and IX show.

Table VIII. Recovery of Uranium by Fusion with NaOH + NaCl

Parts NaOH to 1 part of ore	*Parts NaCl to 1 part of ore*	*% U_3O_8 recovered*
1	0.2	83
1	1	63
2	1	70
3	0.3	80
3	0.3	83
3	2	60
4	0.4	66
5	0.5	66

Table IX. Recovery of Uranium by Fusion with NaOH + NaF

Parts NaOH to 1 part of ore	*Parts NaF to 1 part of ore*	*% U_3O_8 recovered*
0.5	0.1	66
1	0.1	83
1	0.2	86
2	0.2	96
3	0.15	90
3	0.3	93

Potassium bisulfate is one of the best reagents to decompose the zirconium ore of Poços de Caldas. Fusion at 700–800°C is quite convenient for the almost total opening of the ore and leaves only very small quantities of zirconium silicate unaffected. It was therefore thought advisable to experiment with potassium bisulfate as a flux for the solubilization of the uranium of the zirconium ore. Results are shown in Table X. From these tests it can be concluded that using some 10 parts of bisulfate to 1 part of ore, 95% of the total uranium content can be put in solution. Here again it can be remarked that the uranium recovery follows almost proportionally the amount of zirconium ore decomposed.

Table X. Recovery of Uranium by Fusion with Potassium Bisulfate

Parts $KHSO_4$ to 1 part of ore	*% unattacked ore*	*% U_3O_8 recovered*
0.5	95	17
1	87	30
2	71	50
4	63	76
10	27	95

Chlorine attack of the ore at high temperatures, as an attempt to selectively volatilize uranium, failed. Only at temperatures above 1000°C is the process complete and then all chlorides distill off together.

CONCLUSION

In conclusion we can say that though we have in Poços de Caldas a very important potential source of uranium, its recovery is associated with technological problems arising from the intimate association of uranium with zirconium. Technological investigations have been concluded with very promising results for the economical production of uranium for its peaceful use in nuclear reactors.

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Preparation and Separation of Uranium Peroxide, As a Stage in the Chemical Purification of Crude Uraniferous Products

By E. L. Zimmer,* Italy

The purification of uranium salts for the production of high purity uranium metal (for nuclear reactors) is, as a rule, based on the fact that, in most instances, the solubility of uranyl nitrate in organic solvents (particularly ethers and ketones) and the insolubility of uranium peroxide in an acid medium are used in order to achieve very high purification of the crude uranium salts obtained from the products of the chemical treatment of ores (ammonium or sodium uranate, salt of the oxide U_3O_8) by dissolution in acids.

These two operations purify the crude salts to a degree impossible to achieve by conventional chemical purification methods used in industry, which are based mainly on the formation of soluble complex salts with the carbonates. Currently, there is fairly extensive literature on the technique of extracting uranyl nitrate from its aqueous solutions by organic solvents as a separation and purification method. On the other hand, there is a nearly complete lack of data on methods of preparation and separation of uranium peroxide.

The formation of $UO_4 \cdot 2H_2O$ by addition of H_2O_2 to uranyl salts in solution has been known since 1877;[1] however, we know of very few papers in the field of preparative chemistry,[2-5] and almost none at all in industrial chemistry regarding this compound, although today it is rather interesting from a technical standpoint.

At the Bouchet plant, which is working for the French Atomic Energy Commission, the two above-mentioned purification methods are used;[6] in Great Britain, according to an official release,[7] the first purification is carried out in the Springfields plant by H_2O_2 precipitation of a sulfuric acid solution of the uranyl salts obtained by acid leaching of the minerals. The Argentine Atomic Energy Commission has also studied in its laboratories the preparation of $UO_4 \cdot 2H_2O$.[8] A recently published report of the Argonne National Laboratory[9] also contains quite extensive data on the best methods for obtaining $UO_4 \cdot 2H_2O$, as a quantitative analytical separation method.

The chemical laboratory of the CISE group (Milan) made a study of the precipitation and separation of $UO_4 \cdot 2H_2O$, starting from U_3O_8 and crude ammonium uranate, in order to determine practical conditions for preparation, and to note the advantages and limitations of this purification method.

THEORETICAL PRINCIPLES AND PRACTICAL CONDITIONS FOR THE PRECIPITATION OF $UO_4 \cdot 2H_2O$

Uranium peroxide results from the chemical equation:

$$UO_2^{++} + H_2O_2 + 2H_2O \rightleftharpoons UO_4 \cdot 2H_2O + 2H^+$$

the equilibrium of which, under normal operating conditions, is almost completely shifted to the right. So far, little is known of the influence of temperature on equilibrium. The thermal tonality of the reaction, according to the latest thermochemical data[10] was only a few kcal/mole, but it is to be expected, that, at least in a fairly narrow temperature range (about 20 to 50°C) the temperature has no notable effect on equilibrium. It is true that it is possible to re-dissolve $UO_4 \cdot 2H_2O$ precipitated by the action of boiling acid solutions, but it is not easy to distinguish between the effect of reversal of equilibrium caused under these conditions and the spontaneous decomposition (particularly the catalyzed decomposition) of H_2O_2, which obviously favors the redissolution. Patterson[9] points out a few other conditions besides pH (which deserves special discussion) which have considerable effect on the precipitation of $UO_4 \cdot 2H_2O$ salt. In the first place, one can mention the actual solubility of uranium peroxide in water, or better in the salt solution in which uranium peroxide is precipitated. Data for this are fairly contradictory: Mazzucchelli[3] indicates an approximate solubility of 5–9 mg UO_4 per liter in pure water or in a solution of 0.1*M* NH_4Cl. In more concentrated solutions (about 0.5*M* ammonium salts), we have found that the solubility of $UO_4 \cdot 2H_2O$ is often practically negligible: i.e., it is barely possible, if at all, to recognize qualitatively the presence of uranyl salts in solution by a characteristic reaction (for example, by oxyquinoline) in the filtrate which is separated from the precipitates following suitable decantation. Under those conditions precipitation is quantitative: this is also clear from the analytical work mentioned by Duval[11] and the work of Patterson.[9]

Original language: French.
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It has been recognized for a long time that many neutral salts inhibited the precipitation of uranium peroxide; precipitation is retarded or even suppressed in the presence of an excess (how important?) of alkali and alkaline-earth metal salts;[9] it would be incomplete in the presence of large quantities of alkaline-earth chlorides and suppressed by acetates, oxalates, tartrates, sulfates and fluorides present in appreciable concentration.[3,9]

The more or less concentrated mineral acids, particularly when hot, are capable of dissolving $UO_4 \cdot 2H_2O$ partially [4] or totally.[3] Sulfuric acid is particularly noted for this: this is why precipitation in a very acid solution is incomplete[9] or suppressed.[3]

To achieve complete precipitation, it is advisable to use a pH of 0.5 to 3, preferably >1.5, or better, 2 to 2.5.[9] This indeed has been verified by experience.

EXPERIMENTS ON THE QUANTITATIVE PRECIPITATION OF $UO_4 \cdot 2\,H_2O$ FOR THE PURIFICATION OF CRUDE URANIUM SALTS

We have carried out many experiments on the preparation of $UO_4 \cdot 2\,H_2O$ from solutions of crude uranyl salts obtained by dissolution in acids of an impure ammonium uranate or an oxide (U_3O_8) obtained from the latter by calcination at 700–800°C. We have studied the following points, which may affect purification: pH of the solution, uranium concentration, nature of the uranyl salt used (i.e., nature of the mineral acid used to solubilize the insoluble crude compounds), temperature, addition of ammonium salts. We have also endeavored to establish a correlation between the various operational conditions and the structure of the precipitate (particularly the form and dimension of the crystals, which obviously influence the possibility of filtering and washing the precipitate satisfactorily).

The structure of the precipitate varies, particularly as a function of the temperature and pH of the solution. The latter variable is not controlled if uranium peroxide is precipitated by the addition of H_2O_2 to a solution of a uranyl salt: indeed, for a UO_2^{++} ion which disappears from the solution, precipitated in the form of $UO_4 \cdot 2H_2O$, two H^+ ions are formed, i.e., the solution is progressively acidified during precipitation: final acidity being approximately equivalent to the initial concentration of the uranyl salt. Under these conditions at all temperatures between 20 and 100°C and for uranyl salts solutions ranging between 0.1 and 1*M*, there results as we have verified, a very fine light colored lemon-yellow precipitate, which can be filtered, centrifuged and washed only with great difficulty, and which, when wet, has the consistency of a pasty wax. Watt, Achorn and Marley[5], by precipitating at 90°C a 0.1*M* solution of $UO_2(NO_3)$ + 0.1*M* of HNO_3 by an insufficient quantity of H_2O_2, obtained a fairly dense precipitate consisting of small crystals having a cubic habit; at a lower temperature (40–50°C) but with an excess of H_2O_2, they obtained a precipitate having a similar composition but much more voluminous, consisting of very fine needles, conglomerated in microscopic tufts: in the precipitates obtained at a pH$\leqslant$ 1, there would also be a second, unidentified, crystalline phase. This second crystalline phase would not exist in precipitates obtained at pH 2–3.5.

The pH would thus have an evident effect on the crystal habit, and even on the composition of the precipitate; at any rate, we have achieved a heavy crystalline precipitate, which can be filtered, centrifuged, and washed very easily, by adding slowly and with agitation at 40–50°C a small excess of H_2O_2 to a 0.1–1*M* uranyl salt solution; while measuring the pH of the solution during precipitation, and adjusting same to a value of about 2–2.5 by the addition of NH_3 or of sodium or ammonium acetate. Under these conditions, precipitation of uranium peroxide is practically quantitative: one generally finds less than 10 mg of uranium and, in most cases, less than 1 mg of uranium per liter in the mother liquor.

It is to be expected that the quantity of uranium which remains in the mother liquor varies with the composition of the initial solution. We have been able to find a systematic variation of some importance by using solutions of uranyl nitrate, chloride, sulfate, and acetate, with pH initially adjusted to 2.5, and constantly brought back to this value by the addition of NH_3 for the precipitation of $UO_4 \cdot 2H_2O$.

By precipitating in this way a 0.5*M* uranyl nitrate or acetate solution at 18°C, less than 1 mg U per liter is found in the mother-liquor; by precipitating 0.5*M* solutions of uranyl chloride and sulphate, 11 and 23 mg U per liter, respectively, are found after approximately one-hour contact between precipitates and mother-liquors, and much less after longer contact. This would show that chlorides and sulphates suppress or delay precipitation. In reality, the phenomena are a little more complicated, since incomplete and very slow precipitation is observed, which still is not completed after 48 hours, when ammonium sulfate is added to a 0.5*M* uranyl sulfate solution in the proportion of 1 mole per liter, or if the same proportion of ammonium acetate is added to a saturated uranyl acetate solution. The addition of ammonium chloride (1 mole per liter), on the contrary, improves and completes the precipitation of $UO_4 \cdot 2H_2O$, from a UO_2Cl_2, solution, while similar addition of ammonium nitrate has no noticeable effect on the precipitation of uranyl nitrate solutions. Thus, the effect of the ammonium salts depends essentially on the nature of the anion: generally speaking it can be said that the formation of the $UO_4 \cdot 2H_2O$ precipitate is suppressed or retarded by anions which can form complexes with the UO_2^{++} ions (sulfates, acetates), whereas chlorides and nitrates have no noticeable effect. Moreover, this effect of sulfates and acetates would be noticeable only in concentrations higher than about 0.5*M* while the chlorides and the nitrates would have

no appreciable effect, at least up to a solution of about 1.5*M*. When solutions of uranyl salts are neutralized with a sodium or ammonium acetate solution instead of NH_3, no noticeable difference is observed: generally speaking a little more uranium is found in the mother liquors.

PURIFICATION EFFECT ON CRUDE URANYL SALTS DUE TO THE PRECIPITATION OF $UO_4 \cdot 2H_2O$

The precipitation of $UO_4 \cdot 2H_2O$ in an impure solution of a uranyl salt would theoretically leave impurities in solution, and thus would achieve complete purification, except in the case where there would be coprecipitation of sparingly soluble peroxides in a weakly acid medium. This has been verified[9] in the presence of thorium, zirconium, hafnium and vanadium (?). In reality, one must also take into consideration the anions in the solution which might be carried down by the precipitate, despite washings, as well as substances which might be retained by absorption. The $UO_4 \cdot 2H_2O$ precipitate always contains more or less considerable quantities of sulfates (about 1%) when precipitated in sulfuric solution, even after prolonged washing. With soluble colloidal silicon, a noticeable quantity is retained in $UO_4 \cdot 2H_2O$. Phosphates are carried down in the precipitation of $UO_4 \cdot 2H_2O$, particularly in the presence of ferric salts. We have been able to check this by the Scribner spectrographic analysis method ("carrier distillation" in the arc, by Ga_2O_3). A very impure sample of U_3O_8 (prepared by calcination of crude ammonium uranate) revealed, under chemical and spectrographic analysis, a number of impurities, the most abundant of which were: Si, P, Fe, Cu, B, Pb.... The purification by precipitation of $UO_4 \cdot 2H_2O$ by the method described above permits a satisfactory or even almost complete elimination of the following: Ag, As, Al, B, Bi, Ca, Mg, Mn, Mo, Na, Ni, Sb, Sn, Zn.

Elimination was not complete for Cu and Pb (very abundant impurities) and very incomplete for Fe, P, Si (abundant impurities subject to carrier action). This, however, does not constitute a serious limitation of the use of the purification method, since a slight modification of conditions could considerably improve the results. It is well known indeed[9] that ferric salts and copper can be found in a stable complex in a slightly acid medium to make them less detrimental: to this end, it has been recommended that organic acids (acetic, lactic, malonic) be used, and, as a matter of fact, during the operations which precede the precipitation of $UO_4 \cdot 2H_2O$, it is possible to eliminate the major part of the phosphates, the iron and the silicon. These are simple enough operations, and we do not feel that it is necessary to dwell upon them.

ACKNOWLEDGEMENTS

In conclusion, I am glad to extend my thanks to Professor Bolla for his kind interest in this work, as well as to M. S. Terrani, for the spectrographic analysis.

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Extraction of Uranium from Low Grade Yugoslav Ores by Chlorination

By Olga S. Gal,* Yugoslavia

Several low grade uranium ores and other materials containing uranium were chlorinated in the presence of coke as reducing agent. Experiments were performed in a laboratory scale using 5–10 gm samples. Uranium was extracted as gaseous uranium chloride and condensed in water.

APPARATUS

The apparatus consisted of: (1) a commercial high pressure chlorine cylinder, (2) several wash bottles filled with concentrated sulfuric acid as drying agent for chlorine, (3) a flowmeter, (4) a quartz reaction tube of 80 cm length and 4 cm in diameter, which was heated electrically (a Pt-Pt(Rh) thermocouple for temperature control was placed in the tube), (5) several condenser-flasks filled with water. The different parts were connected together in the same order as cited above.

EXPERIMENTAL

Ores were ground and homogenized in the usual way. The particle size of representative samples was determined by granulometric analysis. The same is true of the coke which served as reducing agent. The mixture of ore-sample and coke (usually 10 gm) was placed in the center of the quartz reaction tube, just under the end of the thermocouple. The tube was connected to the other parts of the apparatus and chlorine was passed through it. The temperature was gradually raised to the desired level. The pre-heating time interval (i.e., the time of heating necessary to obtain the desired temperature) was always noted, and afterwards some experiments were carried out to determine its influence upon the reaction. When the desired temperature was obtained, chlorination was continued for one hour; then heating was stopped and the reaction tube cooled under a small stream of chlorine. Uranium was determined in the remaining mixture which did not react as well as in the condensed solution trapped in the condenser flasks at the outlet of the tube. The sum of these two determinations should give, obviously, the initial uranium content of the sample.

The following materials were chlorinated: (1) epidote, (2) schist, (3) roasted schist, (4) coal, (5) ash from coal. Materials 1–3 contained 70–80% SiO_2, 2–4% Fe_2O_3, 10–13% Al_2O_3, 2–9% CaO, 0.5–1% MgO, with losses by ignition 0.5–8%. Materials 4–5 contained 4–12% SiO_2, 10–28% Fe_2O_3, 2–4% Al_2O_3, with losses by ignition 30–85%. The uranium content in all samples was within 0.01–0.05%. Owing to the low uranium concentrations, determinations were made using the well known fluorimetric method.[1] Colorimetric determinations of uranium[2] were sometimes run as controls. Granulometric analysis of the samples (for 100 gm of material and 15 minutes of sieving) gave: (1) Epidote from −10 to 80 DIN 94.79%, −80 DIN 5.21%; (2) Schist from −5 to 60 DIN 76.11%, −60 DIN 23.89%; (3) Roasted schist from −5 to 60 DIN 75.30%, −60 DIN 24.70%; (4) Coal from −10 to 80 DIN 91.83%, −80 DIN 8.17%; (5) Ash from coal from −10 to 80 DIN 86.45%, −80 DIN 13.55%.

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Table I

No.	Material	Ratio sample/coke wt/wt	700°C Yield %	700°C Not extract %	700°C Balance %	900°C Yield %	900°C Not extract %	900°C Balance %	1100°C Yield %	1100°C Not extract %	1100°C Balance %
1	Epidote	1:1	5.5	97.8	103.3	31.7	57.3	89.0	82.8	10.8	93.6
2	Schist	1:1	68.3	18.8	87.1	85.4	9.7	95.1	93.5	8.6	102.1
3	Roasted schist	1:1	46.3	46.3	92.6	73.4	22.2	95.6	93.3	9.2	92.5
4	Coal*	1:1	1.6	74.9	76.7	21.9	59.1	81.0	51.2	35.8	87.0
4a	Coal	1:1	—	—	—	—	—	—	54.1	39.0	93.1
5	Ash*	1:1	12.8	60.1	72.9	45.2	—	—	73.5	10.3	83.8
5a	Ash	1:1	—	—	—	52.3	43.6	95.9	—	—	—

* No coke added, because samples were rich in carbon.

RESULTS AND DISCUSSION

The most important factor in chlorination is the temperature at which the reaction is performed. The economy of the process as well as the choice of materials in constructing the tube furnace depends on this. Thus, the main interest in this work is devoted to the influence of the temperature on the yield of uranium. In all cases chlorinations were carried out at 700°, 900° and 1100°C. The per cent extraction yield was calculated by determining uranium in the condensed solution after extraction with chlorine. The unextracted uranium which remained in the sample after chlorination was also determined and the balance of uranium calculated. The influence of temperature on the yield of extraction is shown in Table I, and graphically in Fig. 1. All results in Table I are average values of 2–4 experiments. As is seen from Table I, the balance is often negative, owing to the loss caused by dissipation in the apparatus, by manipulation prior to analysis, etc.

From these experiments one can conclude that the yield of extraction depends on the kind of material to be chlorinated. Further, in all cases, the extraction is greatly favored by raising the temperature of chlorination.

Several experiments were carried out by changing the following factors: the flow rate of chlorine, the time of chlorination and the ratio sample/coke. Some of these experiments are shown in Table II. It was found that: (1) the flow rate of chlorine, within 10–30 liters per hour, has no influence on the extraction yield, (2) the amount of coke mixed with the sample is not critical; above a certain sample/coke ratio further addition of coke has no influence on the yield, (3) the yield depends on the duration of the reaction. It is possible to find out an optimum time interval of chlorination, where a good yield can be obtained with a reasonable expense of chlorine and heat.

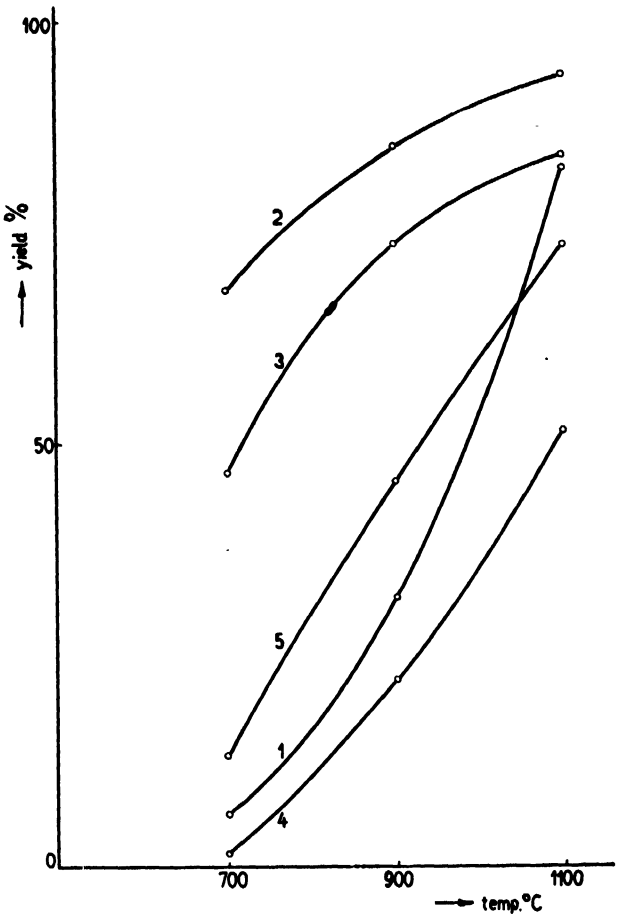

Figure 1. Data for curves are given in Table I, No. 1–5

The pre-heating time, mentioned above, is in some cases an important factor. For example, to obtain 700°, 900° and 1100°C in the tube furnace, pre-heating for about 30, 80 and 150 minutes respectively was necessary. During that time chlorine reacts

Table II

No.	Material	Ratio sample/coke wt/wt	Chlorination in minutes		Flow rate of chlorine, liters/hour	t,°C	Yield %
			Pre-heating	Heating			
1	Epidote	1 : 1	80	60	10	900	37.7
2	Epidote	1 : 1	80	60	20	900	46.6
3	Epidote	1 : 1	80	60	30	900	34.4
4	Epidote	1 : 0.5	80	60	10	900	39.1
5	Schist	1 : 0.5	80	30	10	900	75.2
6	Schist	1 : 0.5	80	60	10	900	93.5
7	Roasted schist	1 : 1	80	60	10	900	59.2
8	Roasted schist	1 : 1	80	60	10	900	73.4
9	Roasted schist	1 : 1	35	0	10	700	38.2
10	Roasted schist	1 : 1	80	0	10	900	53.7
11	Roasted schist	1 : 1	150	0	10	1100	87.6

with the sample and uranium tetrachloride is produced. This was proved in experiments Nos. 9, 10 and 11, Table II. Thus, in some cases, at lower temperature and by prolonged chlorination, the same yield can be obtained as at higher temperature in a shorter time. But in any case, a limiting temperature exists below which no reaction occurs. This limit depends on the material to be chlorinated.

ACKNOWLEDGEMENTS

Thanks are due to Professor P. Savić for his interest and the support he gave during this work.

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The Extraction of Thorium and Uranium from Monazite

By P. Krumholz and F. Gottdenker,* Brazil

A new process[1] is described for the separation of thorium and uranium and for the production of technically pure thorium compounds from crude thorium hydroxide as obtained in the alkaline decomposition of monazite. The process consists essentially of the preparation of highly supersaturated but stable solutions of thorium sulfate and the subsequent crystallization of the sulfate in the presence of ethanol. About 85% of the thorium content is thus obtained as technically pure sulfate. The remainder of the thorium is precipitated as oxalate and, after removal of the greater part of co-precipitated titanium phosphate, is returned to the process. The chemistry of the enhanced solubility of titanium phosphate in solutions of thorium salts and its co-precipitation with thorium oxalate is briefly discussed.

Uranium is recovered from the oxalate mother liquors by precipitating uranyl phosphate at a pH 5 to 5.5. The crude phosphate is extracted with hot sodium carbonate solution and uranium then precipitated with sodium hydroxide as sodium uranate of about 97% purity.

Average recovery is 98 to 99% for thorium and 95 to 97% for uranium, calculated on the original amount in the crude hydroxide.

Monazite, a mixed phosphate of rare earths and of thorium is the chief source of those elements. Its large scale production started with the use of thorium oxide in Auer von Wellsbach's gas mantles, Brazil being the main source of the mineral. With the end of the "gaslight age" thorium lost almost completely its industrial importance but large scale production of monazite continued as several new applications had been found for the rare earth elements. With the advent of the atomic age interest is focused again on the fertile element thorium.

The thorium content of Brazilian monazite varies between about 4% and 12%, 6.5% representing a good average. It contains furthermore small amounts of uranium, averaging 3 to 4% of the thorium content of the mineral. This small amount of uranium has up to now never been explored industrially and its presence even has mostly been overlooked. It will be shown in the following that the economic recovery of uranium from monazite is possible.

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The first step in the large scale production of monazite is the breaking down of the mineral in order to transform it into soluble compounds. Three methods have been developed industrially for that purpose. The most widely used consists of the attack of the mineral with concentrated sulfuric acid. Many variations of this method have been developed and described in the literature.[2] A second method of breaking down is based on the reductive chlorination of the mineral.[3] Little is known of the use of this new process on an industrial scale. The third method, which is almost as old as the sulfuric acid process, consists of attacking the monazite with sodium hydroxide or sodium carbonate, transforming the mineral into water-soluble trisodium phosphate and mixed hydroxides of the rare earth elements and of thorium.[4] The great advantage of the alkali process is that the rare earths and thorium can be freed in one operation almost completely from phosphoric acid, a rather cumbersome operation in the sulfuric acid process. Thorium, on the other hand, may be separated almost completely from the rare earth elements either by selective precipitation of thorium hydroxide or by selective acid leaching of the mixed hydroxides. With suitable pH control uranium remains almost quantitatively with the thorium hydroxide. We decided therefore to adopt the alkaline process for a large scale production of Brazilian monazite.†

As a typical operation of the alkaline process has been recently described in detail,[5] we shall restrict this report to the methods of production of technically pure thorium compounds and to the recovery of uranium, starting from the crude thorium hydroxide as obtained in the alkaline process of monazite decomposition.

The composition of the crude thorium hydroxide from a large scale industrial operation varies within the following limits (calculated on dry basis):

ThO_2	50–65%	P_2O_5	1–2.5%
Rare-earth oxides	2–15%	SiO_2	1–3 %
Fe_2O_3	2–5 %	Acid insoluble	10–30 %
TiO_2	0.1–1 %	UO_3	1.5–2.5%

A great number of methods has been proposed and

† The alkali process has been used in large-scale industrial production (about 2000 tons of monazite per year) since 1949 in São Paulo, Brazil and later on in India.

used industrially[2] for the production of pure thorium compounds from such or similar materials. One of the simplest and most efficient methods of purification consists of the precipitation of thorium sulfate from strongly acid (hydrochloric or nitric acid) solutions.[6] Its drawback results from the use of great quantities of acids and alkalies (for the final neutralization of the former) and heavy corrosion problems. We therefore tried to eliminate those inconveniences, retaining the basic efficiency of the thorium sulfate process.

Thorium sulfate exists in the form of several hydrates, that is $Th(SO_4)_2$ with 2, 4, 6, 8 and 9 H_2O.[7] The 9-hydrate and the 4-hydrate exist in the temperature range between 0° and 100° the only stable forms in coexistence with aqueous solutions of thorium sulfate. The transition point between those hydrates‡ lies near to 47°C.[8] The solubility of the 9-hydrate increases from about 8 gm $Th(SO_4)_2$ per liter at 0° to about 40 gm $Th(SO_4)_2$ per liter at the temperature of the transition point. The solubility of the 4-hydrate, stable at temperatures above 47°, decreases rapidly with increasing temperatures. It is well known that thorium sulfate forms supersaturated solutions and that equilibrium solubilities are reached from both sides very slowly.[7] Such supersaturated solutions may be obtained by dissolving anhydrous thorium sulfate in ice-cold water.[9] Slight warming precipitates the 9-hydrate. The difficulty of preparing anhydrous thorium sulfate and the very great instability of the cold supersaturated solutions make the process unsuitable for an industrial application.[2]

We found, however, that thorium hydroxide (or carbonate) dissolves easily in dilute sulfuric acid with the formation of highly supersaturated solutions, the concentration of which may reach under suitable conditions up to 400 gm $Th(SO_4)_2$ per liter or ten times its maximum equilibrium solubility. Such solutions are most easily formed at temperatures between 45° and 50°, i.e., in the vicinity of the transition point between the 9- and the 4-hydrate. At concentrations up to about 150 gm $Th(SO_4)_2$ per liter, such solutions are stable in the indicated temperatures range for long periods of time, even in the presence of suspended solid particles which normally act as crystallization seeds. It is thus possible to free the thorium sulfate easily and safely from the acid insoluble impurities present in the crude hydroxide. For that purpose the crude hydroxide is suspended in water and 50% sulfuric acid at a temperature of 45° to 50° until the solution contains about 20 gm free H_2SO_4 per liter. The insoluble matter, composed mainly of unattacked mineral, is difficult to filter, but may easily be separated by decantation. By repeating the acid leaching and decantation twice more, thorium and uranium recovery is almost quantitative, less than 0.4% of the acid-soluble thorium material remaining in the residue. The solutions from the second and the third leaching are now used in a counter-current system for the extraction of fresh material.

The supersaturated solution of thorium sulfate obtained in this way, deposits crystals of $Th(SO_4)_2 \cdot 9H_2O$ on cooling. This crystallization is a very slow process. We found, however, that addition of water-miscible organic solvents like ethanol, in amounts of 5 to 15% of the total volume, speeds up the rate of crystallization and lowers the final solubility of the sulfate without seriously affecting its purity. Even under such circumstances, after a crystallization period of three days at 0°, still about 15 gm $Th(SO_4)_2$ per liter remain in solution, i.e., about twice the equilibrium solubility in pure water. This high value is due partly to the slow attainment of equilibrium but also to the increased solubility of thorium sulfate in the presence of complexing agents such as phosphoric acid. The practical yield of crystallized thorium sulfate is about 85 to 88% and thus rather satisfactory. The purity of that sulfate is rather high as compared with the composition of the crude hydroxide. A typical analysis is given in the following:

ThO_2	47 %	P_2O_5	0.045%
Rare-earth oxides	0.05%	SiO_2	0.02 %
Fe_2O_3	0.01%	UO_3	0.01 %
TiO_2	0.02%		

The mother liquor from this first sulfate precipitation contains the balance of the thorium, practically all the uranium and all soluble impurities. Precipitation of this solution with oxalic acid removes all but a very small fraction of the thorium (actually less than 0.5%) together with the greater part of the rare earths and practically all of the titanium and phosphoric acid present in the solution. This thorium oxalate can easily be reconverted into thorium hydroxide or carbonate (by a treatment with sodium hydroxide or carbonate) and returned to the acid leaching. However, all of the titanium and phosphate present is dissolved with the thorium and their presence in high amounts increases strongly the final solubility of the thorium sulfate and decreases the purity of the final product. It is thus necessary to remove the bulk of those impurities before returning the hydroxide to the acid leaching. Two processes have been developed for that purpose. The first consists of a treatment of the crude oxalates with two molar sulfuric acid and enough hydrogen peroxide to convert the titanium into the soluble peroxide complex. Some thorium is lost in that operation. Alternately the crude oxalates may be digested with a solution of oxalic acid which dissolve the titanium in form of the soluble oxalate complex and reconverts at the same time any thorium phosphate into the oxalate. The oxalate so purified is pure enough to be converted into the hydroxide and to be returned safely to the acid leaching process.

The behaviour of the titanium-phosphate system in the presence of thorium is rather puzzling. Tita-

‡ Earlier measurements[7] indicated the transition point was at 43°C.

nium phosphate is very slightly soluble even at high acidities and should thus remain largely in the acid-insoluble residue of the leaching process. The contrary happens actually, titanium passing almost quantitatively into the solution. If this happens, it should be expected that it would remain in the solution if thorium is precipitated as the oxalate. It is, however, co-precipitated almost quantitatively. The reason for that apparently anomalous behaviour is most probably the strong complexing power of thorium for the ions of phosphoric acid.[10] In the presence of high concentrations of thorium salts, the concentration of non-complexed phosphate ions is not great enough to reach the solubility product of titanium phosphate. Thus titanium phosphate is rather soluble in solutions of thorium salts. If, however, thorium is precipitated as oxalate, phosphate-ions are freed and titanium phosphate co-precipitates with the thorium oxalate.

If, after the reprocessing of the thorium hydroxide obtained from the oxalate, the rare earths concentration in the mother liquor of the thorium sulfate crystallizations considerably exceed the thorium concentration, the bulk of the rare earths must be removed. This can be done by a careful fractional precipitation of the oxalates with an insignificant loss of thorium.

About 1–2% of the total uranium content is precipitated with the thorium oxalate and removed in the subsequent digestion with oxalic acid. It was found uneconomical to recover this small fraction of uranium.

The mother liquor contains the bulk of the uranium at a concentration of about 1 gm UO_3 per liter and a large amount of the impurities originally present in the crude hydroxide. Several methods have been proposed for the recovery of uranium from such dilute solutions, mostly based on the reduction to tetravalent uranium and precipitation of the corresponding fluoride, oxalate or phosphate. We found that all those methods remove at best 90% of the uranium. A convenient way to recover almost quantitatively the uranium was found in the precipitation of uranyl phosphate at a pH of 5 to 5.5. Under such conditions 99.5% of the uranium may be recovered in form of a crude phosphate containing about 15% UO_3 on dry basis. A double extraction with sodium carbonate solution at 90 degrees removes easily all but about 1% of the uranium content. Excess sodium hydroxide at 100° precipitates sodium uranate from the solution of the complex carbonate. This is washed alkali-free and dried at 120° A typical analysis of that sodium uranate is given in the following:

UO_3	82 %	P_2O_5	0.75%
Fe_2O_3	0.45%	SiO_2	1.4 %

The new sulfate process described in this paper permits thus a recovery of 98 to 99% of the thorium and of 95 to 97% of the uranium present in acid-soluble form in the crude hydroxide. The thorium is obtained in form of a rather pure sulfate, which can easily be converted into a hydroxide or carbonate and into other thorium salts. The equipment needed for the industrial application of the process is rather simple and needs as construction materials only steel, wood and lead. The efficiency and economy of the process have been proved by a large scale operation, which over a period of 18 months produced several hundred tons of thorium sulfate and several tons of sodium uranate. In not a single case did a premature crystallization of the highly supersaturated solutions of thorium sulfate occur.

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The Possibilities of Securing Long Range Supplies of Uranium Thorium and Other Substances from Igneous Rocks

By H. Brown and L. T. Silver,* USA

It is amply clear that as the nations of the world engage more actively in the accumulation of uranium and thorium, high-grade deposits of these substances will dwindle and man will be forced to obtain his supplies of uranium and thorium from materials which contain these elements in low concentration. If atomic energy were to supply a substantial fraction of the world's power requirements, the drain on high-grade deposits would be particularly rapid, primarily as the result of the huge inventories required for reactor construction. It is quite possible, for example, that power-breeder reactors will necessitate uranium inventories which are over 500 times greater than the yearly consumption of uranium by neutron capture and fission.

Looking into the distant future, it is important that we ask: Can the earth supply inventories of uranium and thorium which may eventually amount to millions of tons? To what extent and at what cost can uranium and thorium be extracted from low-grade materials? Is it within the realm of technological and economic feasibility for a nation which is devoid of high-grade deposits to obtain uranium from substances which exist abundantly on the earth's surface?

In an attempt to answer these questions we have undertaken an investigation of the possibilities of isolating uranium and thorium from one of the "lowest-common-denominators" of the earth's crust —ordinary igneous rocks. Igneous rocks have been chosen for study because they exist in abundance on the earth's surface and preliminary information indicated that uranium and thorium are localized in crystalline rocks in such a way as to facilitate extraction by chemical and physical means.

DISTRIBUTION OF URANIUM AND THORIUM IN IGNEOUS ROCKS

Igneous rocks consist of assemblages of mineral phases which possess diverse compositions and structures. During the process of rock formation, those elements which exist in such low abundance that they are unable to form separate mineral phases, distribute themselves among the major phases in proportions which are determined by the structures of the minerals and by the chemical properties of the elements. Both uranium and thorium possess ionic radii and charges which prevent them from fitting comfortably into the lattices of any of the common major granitic-mineral phases, but they fit into certain of the accessory mineral phases, such as zircon, allanite, sphene and apatite. In zircon, for example, uranium and thorium in the (IV) states can substitute for zirconium(IV).

As a result of these effects, uranium and thorium in igneous rocks appear to be generally localized in mineral phases which make up only a small fraction of the weight of the entire rock. In a granite from Essonville, Ontario, for example, which contains 2.74 parts per million of uranium, over 90% of the element is concentrated in portions of the rock which make up less than 1% of the total weight of the rock, with zircon and sphene retaining the major proportions. Table I shows the concentrations of uranium and thorium in each of the mineral phases of the Essonville granite.[1] From the point of view of the distribution of uranium and thorium, the Essonville granite is probably typical of many granitic bodies scattered throughout the world.

While studying the distribution of uranium and thorium in the Essonville granite, it was noticed that substantial fractions of these elements are chemically so bound that significant extractions can be obtained by leaching the pulverized rock with dilute acid. Experiments with the granite showed, for example, that 29% of the uranium, 42% of the thorium and approximately 40% of the non-radiogenic lead could be readily removed by leaching the pulverized rock for a short time with cold *6M* HCl.

The fact that substantial fractions of uranium, thorium and lead exist in a granite in such a soluble form strongly indicated that other minor elements might be similarly localized. If this were true, there might be a possibility of isolating a variety of products from igneous rock without the necessity of digesting the rock as a whole.

Igneous rocks ranging from tonalites to true granites and of diverse ages and geographic origins, respond rather uniformly to simple acid leaching. The soluble fractions from aliquots of these rocks crushed to pass 30 mesh and leached with *1M* HNO_3 at room temperature for 50 minutes are usually only 0.1 to 0.6% of the original weights. Ca, Fe, Al, Si, P and K are the major constituents

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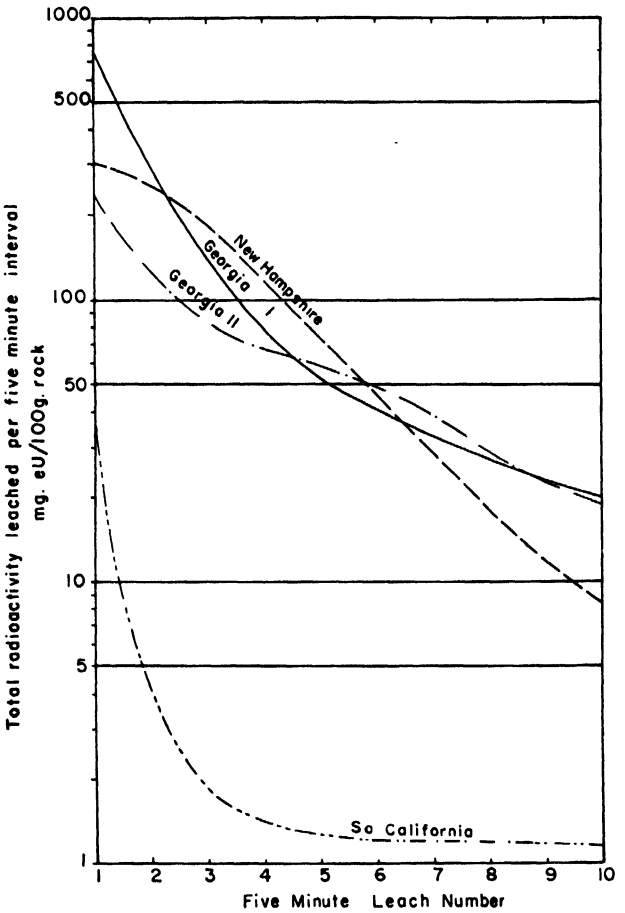

Figure 1. Radioactivity solubility curves for several granites leached with 1M HNO_3 at room temperature

Table I. Distribution of Uranium and Thorium in Granite from Essonville, Ontario

	Mineral abundance (wt. percent)	*Parts per million*	
		Uranium	*Thorium*
Quartz	24	0.130	
Paglioclase	20	0.204	
Perthite	52	0.218	0.410
Magnetite	0 4	2.57	
Apatite	0.02	90.5	
Sphene	0.4	303	5375
Zircon	0.04	2650	2170
Composite rock		2.74	41.88
Acid-soluble material		0.90 (29%)	17.55 (42%)
(micrograms element per gram rock)			

with Na, Mg, Ti, Mn and other elements in the minority. Table II lists the gross composition of leaches from several granites, granodiorites and aplites. They are conspicuously different from the compositions of the rocks themselves.

Uranium, thorium and other rare earths in the dissolved fractions are concentrated 20 to 100 times more than in the original rocks. These fractions may contain up to 40% of the total weight of these elements in the rocks. Weights of extracted U, Th, and rare earth, determined spectrographically, are given for several diverse granites in Table III.

The rate at which the radioactivity is leached from the granites with cold acid is initially quite high and then drops off sharply. Radioactivity solution-rate curves for several granites are shown in Fig. 1. Increased radioactivity solubility rates are induced by higher temperature, but acid consumption from the solution of non-radioactive materials also increases markedly.

The distribution of the acid-soluble radioactivity in granites has been examined by means of alpha-track autoradiographs of thin-sections of rock and through extensive separations, analyses, and rates of solubility studies on individual mineral species or selected mineral assemblages.

The alpha-track studies clearly show that the major portion of the alpha-activity in most granites originates in microscopically visible accessory minerals. A smaller fraction of the activity occurs in the major minerals. Much of this portion appears from the spatial relation to originate in microscopic to sub-microscopic inclusions and imperfections in the coarser granitic minerals. A third type of site for the alpha-tracks is along grain boundaries and fractures where from less than 10% to rarely more than 25% of the tracks may be found. This "interstitial" activity emanates from both microscopically discrete (but identified with difficulty, if at all) and sub-microscopic phases. The "interstitial" phenomena indicate the former existence of a period of mobility for the U and Th in the history of a granite. Such periods may develop in the very late stages of rock crystallization, during a subsequent hydrothermal or metamorphic episode, or during the weathering history of the rock. The distribution of alpha-tracks in thin-section autoradiographs of three granites is given in Table IV.

Table II. Gross Chemical Composition of Leaches in 1M HNO_3 at Room Temperature

Rocks from	*Total solids mg/100 gm*	*SiO_2 Wt %*	*Al_2O_3* Wt %*	*Fe_2O_3 Wt %*	*MgO Wt %*	*CaO Wt %*	*Na_2O Wt %*	*K_2O Wt %*	*P_2O_5 Wt %*	*TiO_2 Wt %*
So. Calif.	470	10	15	27	0.5	22	1.3	14	8.3	1.1
Georgia I	540	4	16	15	..	41	0.9	5.6	17	0.2
Georgia II	310	6.8	17	15	..	35	1.7	4.9	19	0.5
Montana	110	7.4	19	45	1.9	14	3.2	6.9	2.6	..
Ontario	150	3.4	20	47	1.2	12	3.1	8.4	5.3	..

* Includes rare earths.

Table III. Leach Yields from 100-Gram Aliquots of Several Pulverized Granites Treated with 1M HNO_3 at Room Temperature

Granites from	Total solids (mg)	% activity dissolved	% activity U	Weight of trace elements extracted (mg) Th	Ce	La	Nd	Y
New Hampshire	420	25	0.76	4.8	4.4	2.9	2.0	0.12
Colorado	270	15	0.38	1.1	1.6	1.1	0.73	1.0
Georgia I	540	38	0.73	3.0	9.2	5.4	4.3	0.49
Georgia II	310	21	0.50	0.72	3.4	2.3	1.7	0.37

The solubility rate studies of various accessory minerals indicate that a few contribute significantly to the leaches with cold dilute acid. Apatite, allanite (particularly if metamict and altered), thorite, bastnaesite, and a few other species are the principal sources of activity. High degrees of metamictization favor increased solubility. The apatite is responsible for much of the CaO and all of the P_2O_5 in solution, and in rocks where other soluble accessories are absent it is the principal source of activity and rare earths in the leaches. Allanite and highly metamict and altered aggregates which were probably originally allanite appear to be the most important sources of activity in many of the granites examined. The composition of allanite includes most of the major constituents recognized in the leach extractions, even from rocks where the mineral itself has not been identified microscopically. This compositional factor plus allanite's common association with epidote as a deuteric and hydrothermal mineral, and the limited optical data obtained from some of the coarsest "interstitial" material, suggests that allanite may be an important phase in the "interstitial" material in many granites.

PROCESSING POSSIBILITIES

The properties of leachable material, as they have thus far been determined, suggest a number of possibilities for the isolation of uranium and thorium, together with co-products, from igneous rocks. The basic steps would be as follows:

1. Quarry rock, crush and pulverize to grain size.
2. Leach with dilute acid and wash.
3. Neutralize solution and precipitate R_2O_3 group. This precipitate will be composed primarily of Al_2O_3 and Fe_2O_3 and will carry down with it the uranium, thorium, rare earths and the majority of potentially useful trace elements;
4. Allow precipitate to settle, remove supernatant solution and dissolve precipitate in dilute acid. This solution is now sufficiently concentrated to permit direct extraction of uranium, thorium and other useful trace elements by a sequence of straightforward chemical steps.

For the purpose of discussion let us assume that material is being processed which possesses approximately 0.4% leachable matter, corresponding to 4 kg per metric ton of rock. Acid consumption would amount to 40 moles of hydrogen ions per ton of rock processed. Hold-up of liquid in a pulverized rock amounts to approximately 0.3 ml per gram of rock or 300 liters per metric ton. In view of the fact that rates of solution of leachable material drop to low levels below acid concentrations of about 0.1*M* the concentration of the acid should be adjusted so that the hydrogen ion concentration is 0.1*M* after leaching. If one ton of pulverized rock were to be barely covered with 300 liters of 0.23*M* acid, the hydrogen ion concentration would drop to 0.1*M* following dissolution of all leachable matter.

Table IV. Distribution of Alpha-tracks in Thin-section Autoradiographs of Several Granitic Rocks

	Total number of tracks	Major minerals	Accessory minerals	Fractures and grain boundaries
Georgia I	3255	8%	83%	9%
Georgia II	2706	14%	69%	17%
Montana	1034	26%	35%	39%

Utilizing a cycling system involving an initial leach and five washings and using the washings to leach and wash subsequent batches, an over-all yield of leachable material of about 85% could be obtained under steady-state operating conditions. The product-bearing solution would contain about 3.4 kg of dissolved solids (calculated as oxides) per 300 liters, or 11 grams per liter.

The product solution under steady-state operating conditions would have an acid concentration of about 0.063*M*. Somewhat over 60 moles of hydrogen ions and 600 liters of water would be consumed per ton of rock processed.

ENERGETICS AND COSTS

Average granite contains approximately 4 parts per million uranium and 12 parts per million thorium. If all of the uranium and thorium could be extracted from one ton of rock, then converted to fissionable material and fissioned in a nuclear reactor, the energy release would be equal to that obtained from burning about fifty tons of coal. We have seen that on the average about 25% of the uranium and thorium in a granite is leachable and that in an actual process yields amounting to about 85% of the leachable materials can be obtained. Thus, if we assume nuclear breeding and the isolation only of the leachable material, a ton of granite is equivalent in releasable energy content to about ten tons of coal.

We must now inquire into the energy requirements for processing a ton of granite. Clearly, if this were

to be less than the equivalent of ten tons of coal per ton of granite average rock could be processed with a net energy "profit".

We have surveyed the energy requirements for quarrying rock, reducing from haulage size to 10-inch pieces, crushing to 0.25-inch size and pulverizing to less than 50 mesh. It appears that these steps would require somewhere between 7 and 9 kwh per ton of rock. Acids and other chemicals would cost between 10 and 25 kwh per ton, depending upon the acid used (the higher value is computed for nitric acid). Additional direct energy costs including disposal of wastes, water pumping, movement of other materials through the process and maintenance and shop facilities would be about 1 kwh per ton. To these figures we must add the "hidden" energy costs involving original capital investment, replacement of equipment, transportation to and from the plant, etc. These are difficult to estimate, particularly if all hidden energy costs are taken into consideration. However, our calculations indicate that all hidden costs combined might be expected to lie in the range of 0.7 to 2.3 kwh/ton.

These values added together suggest that total energy requirements, both direct and hidden, would probably lie in the range of 19 to 37 kwh per ton of rock processed. If we assume that 1 kwh is equivalent to 1.3 lb of coal burned at 20% efficiency we find that energy costs would lie in the range of 25 to 48 lb of coal per ton of rock processed. This is clearly very much smaller than the equivalent of 20,000 lb of coal which could be extracted from a ton of average rock.

Thus, when we view the problem solely from the energetic point of view, it is clear that most of the granitic rocks of the earth's crust are at mankind's disposal and can be processed for a net energy profit. This means that the reserves of uranium and thorium available to man can be considered for all practical purposes as infinite.

Monetary costs per ton of rock processed probably lie in the range of $1.00 to $2.25 per ton, depending upon the geological conditions and the acid used in processing. This means that if only average granites were processed and no part of the operating cost could be assigned to co-products or to by-products, uranium could be produced at a cost lying in the range of $550 to $1200 per pound. If thorium is considered to possess one third of the value of uranium per pound, the corresponding price ranges would be $270 to $600 per pound for uranium and $90 to $200 per pound for thorium. Values of by-products and co-products would reduce these prices by amounts which are yet to be determined. If by-products valued at about $1.00 per ton of rock could be obtained, as seems possible, the maximum cost of uranium from average granite would be $340 per pound.

It is clear that average granite cannot be processed economically at the present time, but there are large bodies of igneous rocks which possess higher-than-average leachable uranium and thorium contents.

CONCLUSIONS

1. A substantial fraction of the uranium, thorium and certain other elements present in igneous rocks can be readily removed by leaching with dilute acid.
2. More energy can be obtained from average granite in the form of uranium and thorium than is required for the processing of the rock.
3. Although the costs of processing average granite is prohibitively high at the present time, there are igneous bodies which possess higher-than-average concentrations of leachable uranium and thorium. Some of these bodies might well be processed competitively in the near future.
4. There is ample uranium and thorium in the igneous rocks of the earth's crust to power a highly industrialized world economy for a very long period of time.
5. When we look at the situation solely from the point of view of availability, no nation which needs uranium and thorium in quantity need be deprived of supplies of these elements.

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Two Instances of Physical Uranium Ore Dressing

By André Ginocchio,* France

Until now all the uranium deposits being worked in France are of the vein type, and show a great variety of mineralization and structure.

The concentration processes to be used for such minerals have to be devised individually for each of them and, in many cases, only chemical treatment can solve the problem.

In both of the cases described below, however, flotation gave good results.

FIRST CASE

Description of the Ore

It is made up of small parsonsite (uranium and lead phosphate) crystals, disseminated in a quartz gangue. Since the country rock is argillaceous, the mineral as extracted contains 15% to 20% of clay. Accessory mineralization is made up, in variable proportions, of chalcolite, kasolite, and various sulfides (galena, zinc blende).

Parsonsite appears in the form of acicular crystals, which are either elongated or make up curved and extremely friable lamellae, the specific gravity of which varies from 5.35 to 5.40. It crystallizes in the monoclinic system and its formula is: $2\,PbO\text{-}UO_3\text{-}P_2O_5\text{-}H_2O$.

The uranium present in the accessory minerals never accounts for more than a few per cent of the total uranium.

As indicated above, parsonsite is exceedingly friable, and crushing to 0.5 mm yields a large proportion of metal in the fines: 60% in the —200 mesh, of which 20% is in the —15 microns.

Gravimetric Treatment

Following crushing to 1 mm, the mineral was passed on to the shaking table and to a tilting table of the Buckman type.

The results obtained were not too satisfactory, because the average yield varied between 45 and 60%, with a concentration factor of 80 to 100.

Chemical Treatment

In view of the relative failure of the gravimetric treatment, chemical treatment tests were carried out in the laboratory, and their success led to the establishment of a pilot plant.

The mineral was treated at 107°C by a 5% solution of sodium bicarbonate in a pressure vessel (under a pressure of 0.5 kg/cm^2); at the end of two hours, nearly all the uranium was in solution. The leach liquid was re-cycled three times in order to raise its uranium content to a level adequate for a good precipitation

Sulfuric acid then was added to the solution of uranyl carbonate, in order to bring its pH to 2.5, the remaining carbon dioxide was blown off by the injection of compressed air, and the pH then was brought up to 12 by the addition of concentrated caustic soda solution, which gave a precipitate made up of a mixture of uranate and uranium phosphate, analyzing 50%.

The average yield was about 75%, the losses being due to the difficulty in washing the mineral following leaching, due to its argillaceous nature.

Flotation Treatment

Laboratory Tests

Flotation tests were carried out in the laboratory in parallel with the chemical treatment tests.

In view of the argillaceous nature of the mineral, and in order to follow the general practice of flotation of the phosphates with fatty acids, it was necessary first to think in terms of deslurrying the mineral, which would cause a loss of 15% to 20%, giving a final yield only slightly higher than that given by the gravimetric treatment.

Accordingly, it was decided to look into the matter of carrying out the flotation without any deslurrying, and without any heating of the water, another current practice in phosphate flotation.

The results achieved with sodium silicate and oleic acid in the laboratory were rapidly encouraging as to selectivity and recovery, but at the cost of a relatively large consumption of oleic acid (2500 gm/tonne).

Efforts to reduce consumption by lengthening the processing time varying the dilution or the pH, or using fuel oil as a co-collector, were unsuccessful.

Moreover, attempts at using less costly reagents, such as naphthenic acid, talluol soap, and various amines, gave much less favorable results than oleic acid.

A notable improvement was obtained by using a solution of oleic acid in ethyl alcohol; the advantages of this practice being the following:

1. A considerable reduction in the quantity of oleic acid used; under laboratory conditions, it was reduced from 2500 to 800 gm/tonne.

Original language: French.

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2. A decrease in the clay content of the foams.

3. The possibility of avoiding the need for heating the reagent distributors in the winter, as is the case with pure oleic acid.

Under these conditions the following results were obtained:

(*a*) Average first treatment yield 90%, with a concentration factor of 15% to 20%.

(*b*) Average retreatment yield 95%, with a concentration factor of 5.

(*c*) Conditioning time before the first treatment: 10 minutes.

(*d*) Flotation time for the first treatment: 15 minutes.

Flotation is carried out at a pH around 7, but variations in the 6 to 8 range are practically without effect.

We believe it is in order for us to draw attention to the fact that the tests carried out with very pure oleic acid gave worse results than those given by the industrial oleic acids, which shows that a good collector must contain higher fatty acids.

Industrial Flotation

These results, obtained in 1951, led us to substitute a flotation plant for the gravimetric treatment plant; at the same time, various improvements were made at the beginning of the washing section, in particular the installation of a new vibrating screen for 0.5-mm screening.

The flotation shop proper consists of one 100 liter conditioner, one 1000 liter conditioner and eight double flotation cells of the Minemet A 800 type.

The cycle consists of a coarse circuit, using twelve vats, with two consecutive recyclings of the concentrates it gives.

The plant began its activities on February 10, 1952, and met with good success; it operated with the same mineral until May 1954.

In contrast with what happened in the laboratory, the addition of sodium silicate was rarely necessary. The major fraction of the oleic acid-alcohol mixture was added at the intake of the 1000 liter conditioner, after which we made two additions, to the fifth and eighth vats respectively.

Flotation was carried out with a pulp which contained 30% solids by weight, for an average oleic acid consumption of 500 gm/tonne or 190 francs/tonne in reagent cost.

Since the ore content was very variable (from 0.02% to 0.2% uranium), the results achieved were no less variable; the overall yield varied between 60% and 90%, the concentration factors from 40 to 130.

On an average, for two years of operations, the yield was 80% with a concentration factor of 60.

Filtration of the concentrates on a continuous vacuum type filter, proved practically impossible, even following thickening. The addition of various flocculating agents (alum, lime, flocgel) brought about no perceptible improvement; on the other hand aluminum chloride enabled us to achieve a complete transformation of the filtration conditions.

Flotation poisons were the following:

1. Lime, introduced into the ore by residues of the carbide lamps used by the miners. It causes the formation of a very persistent white foam, a bad collector, which cuts the yield in half.

By adding dilute sulfuric acid, it is possible to remedy this poisoning to some extent.

2. Iron sulfates, resulting from the alteration of the sulfides in some parts of the mine, which acts as inhibitors. This inhibiting effect is counter acted by adding sodium silicate, in preference to sodium carbonate.

SECOND CASE

Description of the Ore

The new ore is made up of a mixture, in very variable proportions, of pitchblende, chalcolite, autunite, uranotile, parsonsite and pyrite, the gangues being made up of quartz, feldspars, mica and clays.

The proportion of uranotile (uranium and calcium silicate) is very variable, and the uranium content of this mineral species may reach 30% of the total uranium.

Attempts at Mixed Treatment

Due to the presence of pitchblende (high density) and uranotile (silicate) in the mineral, we have naturally been led to consider the advisability of resorting to a mixed gravimetric-flotation treatment, in order to treat only the phosphates (chalcolite, autunite, parsonsite) by flotation.

By combining or gravimetiric treatment and flotation plants, we carried out industrial tests under the following conditions:

Crushing to sixty mesh, treatment on shaking table of the grains larger than 200 mesh, on Buckman table of the grains smaller than the 200 mesh. The tailings of the shaking table were concentrated in a cyclone, and added to those of the Buckman table, which one could not think of concentrating without incurring the risk of serious losses.

We thus obtained a yield of about 65%, with a concentration factor of 20.

Industrial Flotation

Attempts at direct flotation of this complex mineral by using the olein alcohol mixture gave mediocre yields of about 50%.

On the other hand, the use of an oleic acid-alcohol-Teepol mixture made possible substantially better results.

Under industrial operating conditions, for mineral contents comprised between 0.01% and 0.1%, the yield varies between 60% and 77%, with an average of approximately 70% and a concentration factor of 30 (the flotation circuit is the same as before, namely two recyclings of the concentrates given by the first treatment).

Contrary to what was the case for the preceding ore, the pH had a very important influence on the flotation. It had to range between 6.4–7, and was

adjusted by adding sodium carbonate to the crusher and at various points of the flotation circuit.

Flotation is carried out with a slurry containing 25% solids, at a consumption of 1500 gm/tonne of oleic acid.

CONCLUSIONS

It will be seen, from the examples mentioned above that, although the uranium ores often should be treated by hydrometallurgy, there are cases where flotation may provide a very convenient solution to the problem of concentration.

At any rate, it should be looked into, since it may afford very interesting enrichment with low investments, and still lower costs.

Approximately, it is felt that it is possible to show costs diagrammatically as follows, according to the methods used, taking as a basis the flotation treatment:

	Investment	*Cost, per ton of mineral treated*
Flotation	100	100
Alkaline leach	100	250
Acid leach	300	400

It will thus readily be seen that poor and low tonnage deposits can be worked only following flotation concentration, which makes it possible to write off the facilities on tonnages of only one third of those needed in the case of acid treatment and recovery costs being equal, to treat ores 2.5 to 4 times poorer.

Beneficiation Characteristics of Uraniferous Ores in India

By R. Krishnaswamy, J. Y. Somnay and G. V. Rao,* India

Refractory uranium minerals of pegmatitic origin like samarskite occur in a number of localities in India. The occurrence of these, however, is sporadic, and they are produced only as by-products of the mica mining industry. The placer deposits of monazites are worked for the thorium and rare-earth contents, uranium being a by-product.

Economically workable deposits of uranium are those in which the oxide, hydrated oxide, phosphates, and titanates occur as disseminations in metamorphic rocks. These belong to the pre-Cambrian age, and contain sulphides of copper, nickel and lead. The host rocks are siliceous with little or no carbonates.

The following are some of the deposits which have shown promise of economic exploitation:

TYPE I: FINE TO MEDIUM GRAINED ROCKS CARRYING A FAIR PROPORTION OF SECONDARY MINERALS

(*a*) Chlorite–schists and hornblende–chlorite–schists, containing small quantities of pitchblende and autunite, in association with copper minerals.

(*b*) Chlorite–biotite schists, and apatite–magnetite rocks containing pitchblende, with more or less amounts of gummite and phosphate minerals of uranium.

TYPE II: FINE TO MEDIUM GRAINED ROCKS CARRYING PRIMARY URANIUM MINERALS MAINLY

Phyllites, and the interaction rock carried in them, containing pitchblende and varying small amounts of autunite and torbernite, associated with apatite and copper minerals.

TYPE III: MEDIUM TO COARSE GRAINED ROCKS CARRYING PRIMARY URANIUM MINERALS

Dark grey, fine grained ferruginous quartzites, interbedded with schists, carrying brannerite, besides fair amounts of feldspar, chlorite, magnetite, and minor amounts of limonite and biotite.

In most cases, while the major mineral constituents are liberated at a grind of 100 to 150 mesh, liberation of uranium minerals require much finer grind. Table I gives the constituent minerals in a typical ore, and the unliberated uranium minerals associated with them at a grind of 150 mesh.

The exact nature of association of the uranium minerals with the gangue is not clearly understood in all cases. In some, it has been traced to the submicroscopic cracks and fissures in weathered host rock that have been filled by the secondary uranium minerals.

The formation of these secondary minerals, together with the fact that even the primary mineral occurs as disseminations, tends to concentrate the uranium values in the fines during grinding. The following data are typical of the uranium distribution (Table II).

Since the uranium minerals are not liberated at a reasonable grind and since the grinding is to be kept to a minimum to avoid losses in the slimes, the beneficiation of these ores is carried out to eliminate those minerals which are free from uranium, or those that carry the least amount of it at an economic grind.

BENEFICIATION CHARACTERISTICS OF TYPE I

Hornblende–chlorite schist, occurring in the thrust zone of the Bihar copper belt, is typical of these ores. The major minerals constituting this ore are quartz, hornblende, chlorite, magnetite, with accessory amounts of apatite, limonite, and biotite. Some of the exposed and fractured surfaces carry encrustations of autunite. The quartz grains in the rock are uneven and angular, and contain occasionally inclusions of apatite and magnetite. Biotite, hornblende and chlorite occur as elongated grains with longest dimension in the direction of foliation. Magnetite occurs as small rounded grains, sporadically distributed throughout the rock, and occasionally in patches. Some grains show alteration to limonite. Apatite is well rounded and is usually coarser than quartz. Some of the apatite grains are clear, while others show a greyish brown weathered appearance with numerous cracks. These contain sometimes inclusions of magnetite.

The mineral composition of this ore, and the uranium distribution among the minerals are given in Table I. It can be seen from the figures that gravity processes would not yield a good concentrate with economic recoveries. Table III shows the results obtained on tabling.

Bulk flotation of magnetite, micas and apatite, while depressing silica, is feasible with long chain amines. Table IV shows the results of flotation with Rosin Amine D Acetate (RADA) and with Armac 12–D.

Since the reagents do not have any selectivity for the uranium minerals, some of the liberated grains

* Atomic Energy Establishment, Trombay.

Table I

Mineral	*Wt % of mineral**	*% U_3O_8†*	*% distribution*
Quartz	48.3	0.019	8.3
Micas	32.0	0.170	49.5
Magnetite	16.5	0.216	32.5
Apatite	3.2	0.280	8.1
Free uranium minerals	..	..	1.6‡

* Estimated by the Rosiwal analysis of the powdered ore.
† Estimated by radiometry.
‡ Calculated as the difference between the total uranium oxide in the ore, and that associated with the accessory minerals.

of these are not floated. Some of these, however, could be recovered by scavenging on the tables. In the case of flotation with Armac 12–D, tabling of the flotation tails yielded a concentrate with 0.186% U_3O_8 with an over-all recovery of 3.26%.

Flotation with Armac 12–D, at a grind of 80% —150 mesh, followed by scavenging of the tails on tables produced a concentrate with 0.21% U_3O_8 at an over-all recovery of about 87%. The concentrates contained no quartz but carried most of the other minerals present in the ore. These results are in agreement with what can be expected from Table I.

Table II

Size in microns	*Ore 1*			*Ore 2*			*Ore 3*		
	% weight	*Assay % U_3O_8*	*% distribution*	*% weight*	*Assay % U_3O_8*	*% distribution*	*% weight*	*Assay % U_3O_8*	*% distribution*
+ 72	48.2	0.015	22.6	75.0	0.062	50.2	12.1	0.07	16.0
− 72 + 56	1.4	0.040	1.7	2.8	0.06	1.9	11.9	0.05	9.6
− 56 + 40	6.5	0.014	2.8	6.4	0.11	7.6	33.8	0.03	16.5
− 40 + 28	8.8	0.021	5.7	5.0	0.13	7.0	19.2	0.04	12.5
− 28 + 20	8.5	0.029	7.7	3.4	0.16	5.9	9.0	0.06	8.8
− 20 + 14	6.5	0.030	6.1	2.3	0.24	5.9	4.8	0.13	10.1
− 14 + 10	6.0	0.050	9.4	1.6	0.26	4.5	2.6	0.15	6.3
− 10	14.1	0.100	44.0	3.5	0.45	17.0	4.6	0.27	20.2

Table III

Product	*% U_3O_8*	*% distribution*	*Major minerals*
Concentrate	0.166	14.55	Magnetite
Middlings*	0.067	42.90	Quartz, apatite
Tails	0.126	30.20	Micas, quartz and traces of apatite
Slimes	0.146	12.55	.....
Feed	0.110	100.00	.....

* The middlings contain mainly quartz and carry the least concentration of uranium.

Table IV

Reagents	*Concentrates*		*Tails*		*Feed*
	% U_3O_8	*% distribution*	*% U_3O_8*	*% distribution*	*% U_3O_8*
RADA sulfuric acid	0.205	93.0	0.01	6.90	0.11
Armac 12-D sod. silicate	0.230	83.7	0.03	16.2	0.11

Table V

	% weight	*% U_3O_8*	*% distribution*	
			On heads	*Over-all*
Concentrates	34.4	0.596	63.8	43.4
Tails	65.6	0.177	36.2	25.0
Feed	100.0	0.280	100.0	68.4

It was mentioned earlier that some of the grains of apatite showed weathering while others did not. The secondary uranium minerals are more closely associated with the weathered than with the non-weathered gangue minerals. Recleaning the concentrates in an acidic pulp with certain reagents, notably those of the 600 series of the American Cyanamid Company, does produce a further separation of the weathered and non-weathered gangue minerals. But this does not yield good recoveries as is seen from Table V.

It is clear from the above results that the quartz, forming nearly half of the ore, carries the least amount of uranium. The removal of quartz produces a concentrate with nearly double the uranium values at a loss of about 10–13%. Further concentration is accompanied with much greater losses. The economic upgrading, therefore, stops with the removal of quartz.

There are cases where the rock is not fine grained, and liberation of constituent minerals takes place at a comparatively coarse size, but the uranium minerals are not normally liberated unless the ore is ground to a very fine size.

The ferruginous quartzites, occurring in Bihar carry 0.106% U_3O_8. The major minerals in the ore are quartz and hematite, with accessory amounts of magnetite, chlorite, apatite, biotite, garnet and tourmaline. The radioactive minerals are chiefly associated with hematite. Most of the hematite is

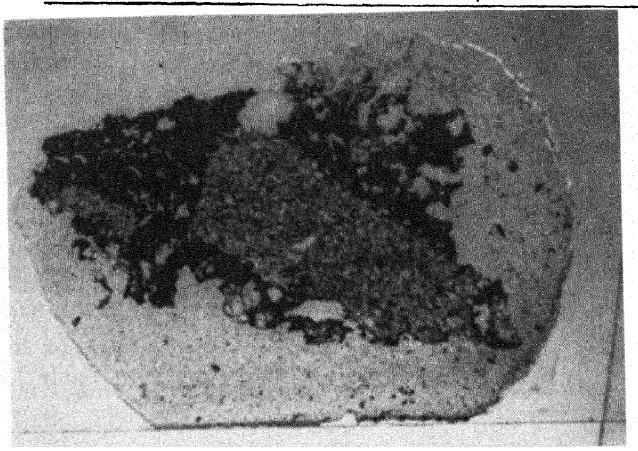

Figure 1. Thin section of ferruginous quartzite, showing hematite and quartz

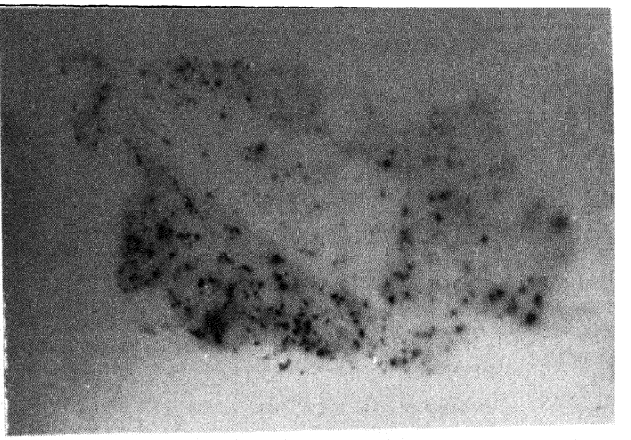

Figure 2. Autoradiograph of section in Fig. 1, showing activity confined to hematite and inclusions of hematite in quartz

liberated from quartz at about ¼-inch size, but for some minute inclusions of it in the latter. Figures 1 and 2 show a thin section and its autoradiograph.

The hematite is highly porous and shows alteration to limonite having a marked tendency to slime. The sliming of the limonite, together with the fact that the uranium is associated with the iron minerals, introduces heavy losses in a straight gravity process. The porosity of the hematite, coupled with the fact that the liberation is effected only at a ¼-inch size, makes conventional heavy media process inapplicable. It is possible that the ore may yield to the more recent methods of heavy media separation, e.g., the Dutch Cone. These, however, have not been tried. The ore yields to agglomeration tabling, to flotation for hematite, and to magnetic separation after a magnetising roast, each of which effects a separation between quartz and hematite.

As seen in Table VI, all these methods yield more or less similar results.

The higher recovery in the flotation and magnetic separation is due to the finer grind when the hematite inclusions in the quartz are also liberated.

Because of the close association of uranium minerals as minute disseminations in hematite, further concentration does not yield good results.

In this, as in the hornblende–chlorite schist, the aim of beneficiation is the removal of uranium-free quartz at an economic grind. The actual choice of the method is controlled by the treatments to follow and economy.

Table VI

Process	*Grind*	*% U_3O_8 in concentrates*	*% recovery*
Agglomeration tabling	—20 mesh	0.25	90.0
Flotation with oleic acid and reagent 801 in acid pulp	—100 mesh	0.24	94.5
Magnetic separation, after magnetising roast at 600°C	—60 mesh	0.24	95.0

BENEFICIATION CHARACTERISTICS OF TYPE II

Where uranium occurs mainly as a primary mineral it has been observed that its association with the gangue minerals is not as close as in the case of secondary uranium minerals. The following Table VII, shows the mineral constituents of a hornblende-chlorite schist, obtained from a depth of about 1200 feet. The rock is essentially the same as the one referred to in Table I, except that the minerals are not weathered. In addition to quartz, micas, magnetite and apatite, the ore carries small amounts of chalcopyrite and pyrite.

Tabling of the ore stage-ground to —100 mesh yielded the results shown in Table VIII.

The concentrate contains mainly the primary uranium mineral (pitchblende) as observed under the microscope and from the autoradiographs. This represents 86.5% of the liberated uranium minerals present at this grind (Table VII).

Further concentration of the uranium minerals can be effected by the removal of sulphides by flotation and apatite by tabling. Table IX gives the results of further upgrading.

Table VII

Mineral	*% mineral in ore*	*% U_3O_8 in mineral*	*% distribution*
Quartz	22.6	0.030	8.5
Micas	57.2	0.018	12.8
Magnetite	7.2	0.040	3.6
Apatite	8.7	0.044	4.8
Sulphides	4.3	0.046	2.5
Free uranium minerals	..	..	67.8

Table VIII

	% U_3O_8	*% distribution of U_3O_8*	*Major minerals*
Concentrate	0.41	59.6	Magnetite, sulphides, apatite
Middling	0.047	31.6	Apatite, quartz
Tails	0.026	8.8	Micas, quartz

Table IX

	% U_3O_8	% distribution* of U_3O_8
Copper concentrate (flotation)	0.046	15.6
Apatite concentrate (tabling of flotation tails)	0.12	9.2
Uranium concentrate (tabling of flotation tails)	1.42	75.2

* The % distribution calculated on the basis of uranium in the rougher table concentrate.

Tabling aimed at the concentration of primary uranium minerals, which are the heaviest in the ore, yields a concentrate of a high grade representing good recovery.

In general, the primary minerals in these low grade ores have undergone alterations and the secondary products so formed have spread to the adjoining cracks and fissures as loose fillings. This secondary alteration, proceeding from the outer shell of the primary mineral grains towards the centre, reduces the inherent grain size of the unaltered primary mineral. The presence of the secondary minerals results in a tendency to slime.

BENEFICIATION CHARACTERISTICS OF TYPE III

Occurrence of brannerite as fair sized crystallites in addition to the disseminations in ferruginous quartzites and phyllites is another case where direct methods of upgrading have shown some promise. It has been possible with this ore to handpick lumps of high activity, indicating the possible applicability of the Lapointe picking belt. Even though the rejects from the above still carry fair amounts of the disseminations of brannerite and require retreatment, the radiogenic picking as a preliminary step seems promising.

Preliminary experiments on electrostatic separation have also shown promise.

SUMMARY

The uraniferous ores in India are almost invariably metamorphic rocks. They carry, apart from the original primary mineral, a number of secondary products, forming encrustations or loose fillings in microscopic fissures and cracks. Milling necessitates fine grinding, thus making all methods involving a coarse feed inapplicable. Because of the complexity of uranium minerals occurring in the ores and because of the extreme fineness of grind required for their liberation, direct methods of concentration of uranium minerals have been of little use, except in isolated instances.

ACKNOWLEDGEMENT

Acknowledgement is made of the results on the infrasizer which have been taken from the tests carried out at the National Metallurgical Laboratory on the same ores by Mr. P. I. A. Narayanan.

Record of Proceedings of Session 14B

MONDAY AFTERNOON 15 AUGUST 1955

Chairman: Mr. B. Goldschmidt (France)
Vice-Chairman: Mr. A. H. de Carvalho (Portugal)
Scientific Secretaries: Messrs. D. J. Dewar and R. Hara

PROGRAMME

P/519	Recovery of uranium from its ores	G. Marvin *et al.*
P/2	Canadian practice in ore dressing and extractive metallurgy of uranium	A. Thunaes
P/339	Method for chemical processing of low-grade uranium ores	P. Mouret and P. Pagny
P/521	Some unusual problems met in the recovery of uranium from a very low-grade ore	M. D. Hassialis and R. C. Musa
P/524	Recovery of uranium from phosphates by solvent extraction	R. S. Long *et al.*
P/784	Recovery of uranium from uranium-bearing alum shale	E. Svenke
P/871	An ion exchange process for the recovery of uranium from carbonate leach solutions	J. Shankar *et al.*
P/977	Some aspects of the chemical treatment of Portugese uranium ores	F. Videira *et al.*
P/986	Acid pressure leaching of uranium ores	P. M. J. Gray
P/997	The South African uranium industry	C. S. McLean and T. K. Prentice

DISCUSSION

The CHAIRMAN: I do not think there would be be any point in my emphasizing the importance of the subject with which we are going to deal today.

As you know, the progress made in treating uranium ore, and especially the very plentiful low-grade ores, will determine not only the supplies of uranium that will be available to us in the future but also the price of that uranium.

I feel that it is worth while noting that the subject of the chemical treatment of uranium ores had until now remained largely secret, and the papers we have received on the subject from a number of countries indicate how unfortunate this secrecy is, since many countries have done the same research work independently. I would mention in particular the recovery of uranium in the form of uranous phosphates, which was a well-known analytical reaction since uranous phosphate is very insoluble. Until recently, at least five or six countries used this process in preparing uranium. The same applies to the use of ion-exchange, and I believe that the recovery of uranium by means of ion-exchange, especially in South Africa, is the first large-scale industrial application in this field.

Finally, I should like to stress the new importance, for many countries at least, of the research on solvent extraction of quadrivalent uranium with phosphoric acid solutions, which will probably allow, or perhaps already allows, uranium to be extracted in the process of superphosphate manufacture.

I think it may be said that virtually no secrets remain in the field of the chemical treatment of ores, and the United States delegation in particular has advised us that it is prepared to discuss freely the findings of American research and development work, as well as the chemical extraction of uranium from its ores.

Thus we may say that we are now about to enter upon a subject in which exchanges of information will become progressively easier, which is very important for us all.

Mr. G. G. MARVIN (USA) presented paper P/519.

Mr. A. THUNAES (Canada) presented paper P/2.

Mr. P. MOURET (France) presented paper P/339.

Mr. M. D. HASSIALIS (USA) presented paper P/521.

Mr. G. G. MARVIN (USA) presented paper P/524 as follows: The phosphate rock mined in Florida and the western States contains an average of 0.01 per cent U_3O_8. Most of the domestic phosphate mined is used in the manufacture of ordinary and triple superphosphate fertilizers. Since the mining and processing of the ore are financed by existing fertilizer production, the cost of by-product uranium recovery is not as high as might be expected.

In triple superphosphate manufacture, about 70 to 90 per cent of the uranium in the rock is solubilized by the H_2SO_4 and reports into the commercial

H_3PO_4 intermediate thus formed. The resulting solution contains about 90 to 200 mg of U_3O_8/liter. Since this is the most economical point in the process at which uranium can be removed, our study has been confined principally to these solutions.

The process for recovery of uranium from phosphoric acid consists of: (1) contacting the acid with a 1–2 per cent solution of an alkyl pyrophosphate in kerosene; (2) separating the phases; (3) recovering the uranium from the solvent as a fluoride salt by precipitation with 48 per cent HF; (4) re-using the solvent on a continuous basis with a required amount of fresh solvent make-up.

A simplified flow diagram is shown in Slide 1 (a full diagram is given in Fig. 1 of P/524). For extractants, we have had most success with alkyl pyrophosphates. These compounds have a high selectivity for uranium over various contaminants. Pyrophosphates with relatively long-chain alkyl groups are virtually insoluble in water but completely miscible in hydrocarbon diluents such as kerosene. Compounds made with alcohols ranging from 4 to 17 carbons have been tested. The extracting power per mole of ester increased with increasing chain length up to twelve carbons, but for economic reasons octyl esters have been used most extensively.

Since pyrophosphate compounds hydrolyze to orthophosphates in time, they should be made in the laboratory within a few days before usage. The hydrolyzed products are less effective extractants by a factor of about tenfold. Thus, a 10–20 per cent solution of octyl-orthophosphoric acid (OPA) is required for uranium recovery comparable to that obtained with 1 to 2 per cent octyl-pyrophosphoric acid (OPPA).

The OPPA solvent is prepared by the reaction of octyl alcohol with phosphoric anhydride. Since the reaction is exothermic, the operation is best carried out in the presence of sufficient kerosene to limit the maximum temperature reached to about 70°C. This can be achieved by use of about one liter of kerosene per mole of P_2O_5. Best yields are obtained if the P_2O_5 is slurried in the kerosene first and the alcohol then added. The reaction is complete after about thirty minutes.

The material thus prepared is diluted to 1 to 2 per cent with kerosene. The purpose of the kerosene diluent is to lower the viscosity of the solution, thus reducing the tendency to emulsify when it is mixed with phosphoric acid. Other common diluents can be used. The choice of diluent has little effect on the resulting extraction.

There is evidence that ions of higher positive charge are more highly extracted by the solvent. Thus, the extraction of uranium is greatly improved by reduction of the solution, which forms tetravalent uranium from the hexavalent form. Iron, which is a major contaminant, is also reduced from the highly extracted ferric state to the poorly extracted ferrous state. Most commercial H_3PO_4 has an emf of −240 to −300 mv. In this range, maximum extraction coefficients of about 10–15 are found with 2 per cent OPPA. If the solution is reduced (0 to −100 mv), the coefficient is increased to about 200.

This is simply shown in Slide 2 (Fig. 2 of P/524). Because the maximum amount of uranium that can be extracted is limited by the amount of extractant present, the value of the extraction coefficient drops as the concentration of uranium in the organic increases.

It has been found that the solution can be reduced most economically with scrap iron. The solution can be contacted with the iron either in a batchwise manner or continuously in a column. About 4 grams Fe/liter is generally required for complete reduction. Reduction is needed only if the emf is more negative than −300 mv.

The OPA extraction coefficient is adversely affected by increasing phosphate concentration. The coefficient varies with the inverse fourth power of the phosphate concentration. With OPPA, the effect of phosphate is smaller. Extraction is also affected by temperature. For example, the extraction coefficient at 50°C is only about 30 per cent of that obtained at 25°C with either OPA or OPPA.

Any desired degree of extraction can be obtained by proper adjustment of such operating factors as concentration of OPPA in diluent, feed ratio of solvent to acid, and number of stages used in the extraction. Increasing any of these increases the extraction.

Although several types of contactors can be used, most of the counter-current experiments were done with mixer-settlers. Mixer-settlers give higher stage efficiencies than other types of extraction equipment, and recovery of the solvent for further treatment is simple. In a four-stage counter-current mixer-settler at a 10:1 flow-rate ratio of aqueous to organic, 2 per cent OPPA was required for 90 per cent recovery of uranium from unreduced feed acid, but only 1 per cent OPPA was required for the same recovery from reduced acid. These extractions were obtained on acid containing about 30 per cent P_2O_5. About five minutes of mixing time and five minutes of settling time were employed in each stage.

The uranium can be precipitated almost quantitatively from OPPA by contacting it with about 1 to 1½ lb HF per lb of U_3O_8. The HF is best applied as a 48 per cent to 60 per cent solution. Higher concentration results in excessive deterioration of the solvent. Lower concentration causes emulsion. Contact time need be no greater than fifteen seconds.

The product thus obtained is a uranous fluoride containing about 50 per cent U_3O_8, with fluoride, phosphate and iron as the major contaminants. Some phosphoric acids contain small amounts of rare earths. These are extracted with the uranium and result in cakes containing about 5 per cent rare earth oxides.

The HF partially hydrolyzes the pyrophosphate and reacts to some extent with orthophosphates. For OPPA, a two-minute contact with HF lowers the

extraction coefficient to ¼ its original value, and an 18-hour contact to $\frac{1}{40}$ of its original value. In order to restore the organic to its original extracting ability, a make-up of 50 to 100 per cent of the original amount of OPPA used is required, depending on the conditions of extraction and stripping. It appears that extraction after continued usage is due to both the OPPA and the OPA components. The latter is present because of the decomposition of the former.

The process for uranium recovery from H_3PO_4 as I have described it has been investigated extensively in the laboratory. Acids from about twelve different commercial sources have been tested, but no significant difference was noted. The laboratory work was followed by pilot-plant testing. Finally, several full-scale plants using this process have been built.

Mr. E. SVENKE (Sweden) presented paper P/784.

Mr. J. SHANKAR (India) presented paper P/871.

Mr. P. VIDEIRA (Portugal) presented paper P/977.

Mr. R. G. THOMAS (Australia) presented paper P/986 and added in relation to the fifth paragraph of that paper: This mineral was named after Sir Edgeworth David, and very appropriately so. He was a geologist with a wide range of knowledge of many things, so that this mineral, with its wide range of composition, seems to be very appropriately named. In the sample in the exhibition here, it is stated on the label that it is said to contain the ingredients listed. I can assure you that it does contain them, and in fact it contains many more which are not listed on the label.

Mr. T. K. PRENTICE (South Africa) presented paper P/997 as follows: With the advent of this atomic age and the consequent world-wide search for uranium, the ores of the South African gold mines were investigated, and it was found that virtually all of the ores contained uranium in relatively small concentration. It was found also that the vast tonnages of gold metallurgical plant residues which are lying on the surface and which have accumulated over several decades carry a somewhat similar uranium content. Since the rate of milling of current gold ores is of the order of 5,000,000 tons per month, it was soon realized that South Africa possessed a large potential source of uranium. Moreover, this was a source of uranium which would continue, with current gold mining, over very many years.

Steps were immediately taken to determine whether or not the uranium, existing in the tailings from our gold plants, could be recovered on an economic basis.

Various methods for the dissolution of the uranium from these tailings were investigated, including alkali leaching, and sulfuric acid leaching, and it was decided that the best results could be obtained with sulfuric acid leaching in the presence of an oxidizing agent.

Prior beneficiation of the tailings by means of gravity and flotation concentration was investigated for the purpose of reducing the tonnage to be leached with sulfuric acid, and it was found that by means of flotation concentration it was possible to recover uranium at a much lower cost per pound but with a considerable reduction in the over-all percentage recovery. However, maximum output in the shortest possible time was the overriding issue at that time, and it was therefore decided to adopt the procedure of submitting the total ore to an acid leach under oxidizing conditions.

Having decided upon the method of dissolving the uranium, the next question was how to separate the uranium-bearing solution from the treated slime. Consideration was given to countercurrent decantation, but it was decided to use rotary vacuum filters with which considerable experience had already been gained in the gold reduction plants. It was found, however, that the slime, which for gold recovery purposes is usually ground to over 70 per cent — 200 linear mesh, was difficult to filter after agitation with sulfuric acid solution, and it became necessary, as stated in the paper, to resort to a filtration-aid in the form of animal glue. It was found also that to obtain a satisfactory separation of the uranium solution from the treated solids, it was necessary to adopt a primary and a secondary filtration step. In this system, the slime from the primary acid filters is repulped with a very dilute acid solution virtually free of uranium and refiltered; the residue cake therefrom is discharged to waste and the filtrate solution is used to repulp the slime entering the uranium plant, and as the wash on the primary acid filters.

Consideration was then given to the method to be adopted for the recovery of the uranium from the filtrate from the primary acid filters. Chemical methods of precipitation were tested and one of these methods might have been adopted but for the advent of the application of ion-exchange to uranium solutions in 1950. The latter method was then tested and, although not much was known about it at the time, it gave sufficient promise to justify its adoption. At that time we were unaware of the tributyl phosphate solvent process which is being demonstrated at this Conference in the American exhibit.

In a few words, then, the process of uranium recovery upon which we decided comprises a single acid leach followed by two-stage filtration, and the application of ion-exchange for the recovery of the uranium from the acid solution.

Having proof that we had a reasonably satisfactory process for the recovery of uranium from South African gold ores, we were in a position to negotiate a contract for the sale of uranium, and this contract was entered into at the end of 1950 on the basis referred to in the paper.

The terms of the contract preclude me from giving details of grade of ore treated and details of the extraction process, but in the paper we have described the metallurgical flow-sheet as far as we were

permitted. I have no doubt that as a result of this Conference the restriction to which I have referred will soon be removed, and we will then take steps to publish in an appropriate technical journal a full description of our process, together with recovery statistics.

Having a signed contract for the disposal of our uranium output, we were then faced with the installation of several relatively large uranium plants at a time which coincided with a period of remarkable mining and industrial activity in South Africa and, when account is taken of the fact that the recovery plants had to be constructed almost throughout with acid corrosion-resisting material, we believe it was no mean achievement to have the first plant in full operation by October, 1952. Other plants came into production soon afterwards and we have now twelve large recovery plants in production and will have three more in production by the middle of 1956. The average cost of a plant with a capacity of 100,000 tons of ore per month is about £3,000,000.

These plants were installed on those mines which promised the best economic recovery of uranium and, of course, much of the ore at present being milled in our gold plants is not being treated for uranium recovery. Whether or not more plants will be installed will depend upon the demand for uranium.

When we decided upon uranium recovery there was virtually no excess sulfuric acid available in South Africa for this new industry, and it has been necessary to build seven large contact-acid plants with an over-all daily capacity of 1340 tons of sulfuric acid. The combined cost of these plants is of the order of £7,000,000. Nor was there a source of sulfur for these acid plants, but we were fortunate in that the gold ores contain, in many cases, sufficient pyrite of the order of 2 to 5 per cent FeS_2 to render its recovery by flotation economically justifiable. Pyrite flotation plants of an aggregate cost of about £2,000,000 were therefore installed, and all of the pyrite required for acid production for the uranium industry is being, or will be, obtained from the treatment of gold ores.

We were fortunate, too, in that we had a supply of manganese ore not far from our uranium plants. Initially we thought that the manganese ore reserves would be inadequate to meet the requirements of the uranium industry and we therefore installed, with each uranium plant, a subsidiary plant for the recovery of manganese dioxide from the waste solutions as described in the paper. These have not given as good a recovery of manganese dioxide as was expected, but it now appears that the supply of new manganese ore will be adequate to meet our requirements.

Our uranium plants are giving a performance close to that predicted from initial pilot plant investigations, and very few teething troubles have been experienced. It was found that, whereas relatively coarse particles of sand can easily be held in suspension in an alkaline pulp of a ratio of one of solution to one of solids, these particles settled rapidly in an acid pulp of the same liquid to solid ratio. This necessitated the speeding up of the agitation rakes on the rotary filters, and this difficulty was soon overcome.

We have found also that, whereas we normally treat the slime at atmospheric temperature, improved dissolution is obtained by increasing the temperature by injecting steam into the pulp-agitators. It has been found that the addition of the steam does not, as one might expect, materially dilute the pulp under agitation.

We have to ensure that all of our effluent solutions are adequately neutralized before being discharged to waste. For this purpose lime is used.

We have obtained material benefit from the prior filtration of the alkaline slime as it leaves the gold plant before passing the de-watered slime into the uranium plant because this has considerably lessened the trouble we otherwise would have experienced in the ion-exchange columns due to the presence of cobalticyanide in the gold residue solutions.

DISCUSSION OF P/519, P/2, P/339, P/521, P/524, P/784, P/871, P/977, P/986, P/977

The CHAIRMAN: The first question has been put by Mr. D. N. Wadia (India): "Do I understand that the ordinary beneficiation practices in ore dressing are now given second place in the treatment and concentration of uranium ores?"

I think the answer is in the fifth paragraph of Mr. Marvin's paper, where we find:

"In summary only a few ores being processed for uranium have been found amenable to physical beneficiation techniques. However, we have no reason to believe that physical beneficiation is not an economic possibility and we are continuing our efforts to develop commercially attractive techniques."

Does this reply satisfy Mr. Wadia?

Mr. WADIA (India): Yes. Thank you.

The CHAIRMAN: Mr. Videira (Portugal) asks of Mr. Thunaes (Canada): "What is the U_3O_8 content of the concentrates obtained by direct precipitation with magnesia?"

Mr. THUNAES (Canada): The U_3O_8 concentrate obtained by direct precipitation will vary a great deal depending on the type of ore. If you have a very siliceous ore you will get a high-grade precipitate; you may get 10 to 15 per cent. For other ores it may be as low as 2 to 3 per cent.

The CHAIRMAN: I would now like to ask Mr. Thunaes a question myself: What is the ratio of thorium to uranium in the Bancroft ores containing uranothorite?

Mr. THUNAES (Canada): In the Bancroft ores the ratio varies somewhat. I suppose the ratio may be of the order of 1 thorium to 5 uranium for the over-all ore, but the ores contain uraninite as well as uranothorite. However, I am not certain of the exact composition of the mineral.

The CHAIRMAN: This question is of much interest to us in France, as we are now treating an ore from Madagascar, uranothorianite, which contains about seven parts of thorium to one of uranium. This ore is almost pure thorium oxide with uranium oxide as the main impurity.

And now here is a question asked by Mr. Roques (France): "Why did you abandon gravity concentration at Port Radium?"

Mr. THUNAES: (Canada): The gravity concentrates at Port Radium are still being maintained on a small scale. The ore from the mine is still being treated by jigs. The tailing from this jig concentration goes to the jig plant along with reclaimed tailings from previous concentrates.

The CHAIRMAN: Mr. Roques has also submitted the following question: "Has any attempt been made to use the flotation method at Port Radium?"

Mr. THUNAES: (Canada): Yes, we tried for some time in the early stages of our research to float the Port Radium ore; however, we have not been successful.

The CHAIRMAN: The third question of Mr. Roques deals with details of this flotation. If you have not been successful, however, I will not put the question.

Several questions have been submitted by Mr. J. Mabile (France), and I will begin by reading the first of them: "Is the Lapointe process of electronic concentration widely used?"

Mr. THUNAES (Canada): No. The picker-belt, as we call the electronic concentration method, is not used on a commercial scale. We have run a great many pilot plants on this method, but so far it has not been used on a large scale.

The CHAIRMAN: Now here is Mr. Mabile's second question: "Does this process use scintillometers or Geiger counters?"

Mr. THUNAES (Canada): You can use either scintillometers or Geiger counters.

The CHAIRMAN: I feel that we could pass over the next two questions as they refer to the industrial application of the process, and Mr. Thunaes has just told us that there is no practical application in industry. Mr. Mabile asked what was the concentration obtained industrially as a function of the size of the grains, but I do not think it is used industrially.

Mr. THUNAES (Canada): I believe that the question concerns the various grades of reject at various sizes. The reject assay will generally be found to be higher for the lower sizes, say 1 inch, compared to the 3, 4 and 6-inch sizes. Normally, in most ores, they are of the order of 0.02 per cent to 0.03 per cent U_3O_8 in the rejected waste product.

The CHAIRMAN: Mr. Mabile has another question on the Lapointe process. He asks how it compares with classical methods of preconcentration, from the point of view both of capital required and of cost of production.

Mr. THUNAES (Canada): I am afraid that is a very large question to answer in a few words. There is a limitation on electronic sorting. You can only reject about 30–40 per cent of the ore. You can usually make a much better ratio of concentration by heavy media separation. We do not know the actual cost of electronic sorting because we have not used it on a large scale. We have only estimates; they will not be of much use. We believe it might be somewhat cheaper than heavy media separation.

The CHAIRMAN: I am now going to reply myself to questions that Mr. Videira asked of Mr. Mouret. The first question is: "Is the process applicable economically to 0.5 per cent free U_3O_8, or more?" The answer is that we are employing this process economically with ores with a content of less than ½ per cent; we could therefore use it still more economically with ores having a concentration of more than half of one per cent.

The second question is: "Does the aluminum precipitate in the precipitate?"

We get very little aluminum carried in the uranyl phosphate.

There is also the following question put by Mr. Mouret to Mr. Marvin: "In the extraction of uranium by ion-exchange in the presence of resin, what is the grain size of the ore and of the resin and what is the consumption of resin per ton of ore treated?"

Mr. MARVIN (USA): I think that question can best be answered by referring to paper P/526, the resin process for the recovery of uranium. It is a lengthy paper of 25 pages, and I believe it covers what you wish to know. It is not discussed here, and I do not think I can give you actual figures off-hand, but I can give approximate figures if you would like those. I believe it is in the paper.

The CHAIRMAN: Here is another question for Mr. Marvin, this time from Mr. S. V. Guédès (Brazil): "Is any process being applied to treat the complex ores containing pyrochlore minerals?"

Mr. MARVIN (USA): We have investigated only on a very small scale some pyrochlore from Africa. It was of very low grade. The English at Teddington have done more work on it than we have. It has been dropped because it did not appear to be feasible. I have no positive or encouraging results on the pyrochlore minerals.

Mr. F. A. FORWARD (Canada): Perhaps I might say a word or two about two aspects of the discussion this afternoon. One matter was mentioned by several authors: Mr. Marvin, Mr. Grinstead (P/522) and Mr. Shankar in connection with the precipitation of uranium from carbonate solutions using hydrogen. I think it might be interesting to remark that that has been carried out on a pilot plant scale in a plant treating about half a ton to one ton a day of uranium ore, and the conditions of operation were very much easier to set up than has been indicated or than most people have thought of. My recollection is that the precipitation was carried out very readily from ura-

nium solutions containing about one gram per liter of uranium at 120°C with approximately 8–9 atmospheres of hydrogen pressure, a total pressure of about 10 atmospheres. An advantage of course was that it was possible to strip the uranium completely from the carbonate solution in a very short time, and the variable that governed the rate of precipitation was really the amount and kind of nickel catalyst used rather than temperature or pressure or any of the other factors.

The second point I wish to say a word about is in reference to the paper presented by Mr. Thomas describing the acid pressure leaching of uranium from ores. The impression was left from reading the paper, I think, that it is necessary to use oxygen at very high pressures—the figure of about 500 psi was given—to extract uranium from ores and to effect the oxidation of the pyrite. The fact of the matter is that it is not necessary to do that at all. The work that has been carried out actually again in a pilot plant dealing with about half a ton to one ton a day shows that it is quite unnecessary to use high pressures, but that oxygen pressures of the order of 10 psi, which is about one atmosphere oxygen pressure, or if we include the nitrogen in the air, five atmospheres of compressed air permit this operation to be carried out; and that temperatures of the order of 140°C to 150°C are quite high enough. That means the total pressure necessary to operate such a process is under ten atmospheres, and hence well within the range of ordinary commercial equipment. I think perhaps what Mr. Gray has done is to mistake the effect of agitation—which is extremely important—as he has used a small rocking autoclave. If you use another type of agitation in the autoclave, the pressures come down and the operation is much more easily carried out.

Mr. B. TEZAK (Yugoslavia): I would like to make some comments on papers where the question of precipitation is mentioned. My remarks concern the effectiveness of the chemical precipitation technique for the recovery of uranium from digest liquors. Besides various conditions which have been mentioned and which should be taken into account for the effective chemical precipitation, the role of the concentration of the precipitating components, as well as the influence of the various salts in the liquor—it may be neutral salts present in the liquor—are very important. Especially is this so when the problem of precipitation components in low concentration is encountered. If the Chairman would allow me, I would like to show some slides where such effects are illustrated.

In Slide 1 (See Fig. 1 of P/991, Session 10B.3, Volume 7, these Proceedings) we have a precipitation system of uranyl nitrate $1 \times 10^{-2} N$. On the abscissa we have a logarithm of the concentration of sodium hydroxide. You can see, if we have such a concentration of uranyl nitrate, that is about one gram of uranium per litre, we may obtain the precipitation with the concentration of sodium hydroxide higher than about $1 \times 10^{-1} N$.

In Slide 2 (Fig. 10 of P/991) we have a similar diagram where the tyndallometric values are given as ordinates; the tyndallometric curve presents the amount of the precipitate formed. The abscissa gives the concentrations of the ammonium carbonate and it can be seen that by changing the concentration of the carbonate a very significant maximum is obtained. By following the concentration of the uranium contained in the liquor, you will see that it corresponds to the maximum. This curve shows the percentage of the uranium in the mother liquor and in maximum about 20% is left in the solution

Slide 3 (Fig. 12 of P/991) shows that the effect of neutral salts is very great. With concentrations of sodium nitrate higher than $1 \times 10^{-1} N$ we have precipitation. A similar but more effective influence of magnesium, calcium, barium, and lanthanum should be noted.

The critical relationship in the system of uranyl nitrate–barium chloride–sodium carbonate components is given in Slide 4 (Fig. 13 of P/991).

The CHAIRMAN: I have a feeling that this is not entirely relevant to the subject with which we are dealing today. It has more to do with the analysis questions which we shall be discussing tomorrow.

Mr. TEZAK (Yugoslavia): Yes, but it is very important also to have in mind all similar relationships when one is dealing with various ores and various concentrations of critical components. With small concentrations it is doubtless preferable to work in the regions of the precipitation maximum mention. More details may be found in paper P/991.

Session 15B.1

PRODUCTION OF METALLIC URANIUM AND THORIUM

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Production of Uranium Metal

By L. Grainger,* UK

The bulk supplies of uranium required for the British atomic energy project have been produced at the Springfields Works near Preston, Lancashire, first under the Ministry of Supply, and more recently under the United Kingdom Atomic Energy Authority. When the Production Division of the Department of Atomic Energy was set up in February, 1946, it had the two primary objectives of designing and constructing BEPO and of producing plutonium. It was clear that the construction of a complete factory for manufacturing uranium metal from ore was extremely urgent.

At this time some work had been carried out by I.C.I., under contract, to develop methods for producing metal from pure uranium oxide, which was then available from the United States and this work was approaching completion. No development of the processes to convert virgin ores to pure uranium oxide had been carried out, however, and it was now necessary to provide for these stages also.

Although a basically simple process was finally selected, the urgency of the project and the special difficulties strongly influenced the choice of process and the detailed implementation. In the first place, since it was desirable not to spend time developing a new site, an existing wartime chemical factory was selected. This enabled much effort to be spared from the construction of road and rail connections, workshops, stores and services and, in fact, by the exercise of some ingenuity it was found possible to house many of the processes for uranium manufacture in buildings previously used for other chemical processes.

A grave difficulty which existed was that only a modest amount of technical information was available on the processes selected, and this mainly on the laboratory scale only. Time was too short to await further research work on these processes and their development on a semi-technical scale and it was decided to proceed immediately to the design and construction of the full-scale plant without intermediate development work. The shortage of research and chemical engineering information had one important effect on the design of the factory. It is much more difficult to scale up from laboratory bench work to a continuous process on the industrial scale than it is to scale up to a batch industrial process. For this reason batch processes were adopted in most stages in the design of the Springfields Factory.

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A third difficulty was that the purity of the final product had to be far higher than is usual in industrial chemical processes. This demand for high purity had to be met by a very careful consideration of the specification for the reagents to be used in the manufacturing process, and by equally careful consideration of the properties of the materials used in construction of plant and equipment, to ensure that they did not give rise to pollution.

The last and perhaps the most important difficulty lay in the fact that never before had a factory been built in the United Kingdom in which radioactive material would be handled on the scale of several hundred tons a year. There was at that time little experience available to British industrial medical officers to enable them to give guidance in the design of the plant. It was necessary, however, for them to specify, amongst other matters, the conditions under which massive uranium could be handled and a tolerance for uranium dust in the atmosphere. It is now clear that the tolerances then properly set were very much on the safe side, but they strongly influenced plant design and operation since the figures stipulated could be met only by exercising the greatest care. It was decided, for example, to carry out as many operations as possible in the wet; where dry salts had to be handled special cabinets or ventilation were provided.

EXISTING PROCESS

In outline, the process used at Springfields for the manufacture of uranium metal is first to crush the ore and to dissolve this in mixed sulphuric and nitric acids. The solution is filtered to remove impurities and the uranium is precipitated as a crude peroxide. This peroxide is redissolved in nitric acid and passed through a solvent extraction process to remove the remaining impurities. The purified material is precipitated as ammonium diuranate and converted into uranium tetrafluoride, which is reduced to the metallic form.

Ore Crushing and Sampling

The ore, consisting of fine powder, granular material, or lumps up to 8 in. in diameter, arrives in drums and contains a certain amount of radium and radon. Any radon released on opening the drum is taken up and discharged from the stack of the ventilation system. The ore is tipped into a hopper and fed to a jaw crusher. The discharge from this passes to a screen, oversize material being fed to a cone

crusher and returned to the screen after reduction to about ¼-in. mesh.

Sampling of the ore is a matter of great importance because the price paid is based on assay. The sample is taken by feeding the crushed ore to a series of four Vezin samplers which continuously remove a proportion of the feed. The final sample is pulverised in a disc grinder and emerges as 80 British Standard mesh material. It is then coned and quartered to give a number of samples for distribution to buyers' and sellers' representatives for analysis.

The whole of this crushing and sampling process is done in plant which is not approached while it is in operation. Ventilation of the plant is achieved by two powerful fans which draw air from numerous points through cyclone dust separators and discharge through an air scrubber to a high level stack. The air scrubber is sprayed with water circulating in a closed system; dust removed from the ventilation system is recovered from a labyrinth, drummed and returned to store.

Extraction

The crushed ore is slurried with water, reduced to about 30 mesh in a ball mill and discharged into a stirred stock tank. The slurry is fed at a controlled rate to the first of three cascade dissolvers, stainless steel tanks fitted with stirrers, to which nitric and sulphuric acids are added continuously according to the uranium content of the slurry. Heating is by live steam, and radon and acid fumes are efficiently extracted. The slurry overflows from the first to the second dissolver, which is also heated, and barium nitrate solution is then added to form insoluble barium sulphate and co-precipitate the radium present as sulphate. The mixture then overflows to the third dissolver where it is cooled by a cold water coil, causing further separation of insoluble sulphates. It is then pumped to filter presses which retain all insoluble materials, including the radium and precious metals.

Purification

The uranium in the clear liquor from the presses is next precipitated as uranium peroxide by the addition of hydrogen peroxide under carefully controlled conditions of acidity and temperature and is removed from the solution by filter pressing.

The crude oxide is re-dissolved in warm nitric acid to form uranyl nitrate solution. The final free acidity and specific gravity of the solution are carefully adjusted within prescribed limits, and the solution is then evaporated under reduced pressure until it reaches the composition of uranyl nitrate hexahydrate.

The molten concentrate is then pressure filtered through fine gauze to take out some of the impurities, and further purified by a single-stage ether extraction. The majority of the uranium is dissolved in the ether, while the bulk of the impurities remain in the aqueous layer which falls to the bottom of the extractor and is run off continuously to stock tanks. The ether layer is then washed with a small amount of warm demineralised water to remove most of the remaining impurities, and finally treated with a large volume of cold demineralised water to wash back the uranium into aqueous solution.

Preparation of Uranium Tetrafluoride

The pure uranyl nitrate solution from the ether purification plant is treated with ammonia to precipitate ammonium diuranate. The yellow precipitate is washed with water in the precipitator and dropped on to a Nutsch filter. Vacuum is applied under the cloths, producing a semi-dried cake which is filled into trays for use in the "Dryway" plant.

It should be noted that at this stage the uranium reaches its highest purity. Up to this point in the process impurities have been progressively removed from it; after this stage it inevitably picks up some impurities from the plant and apparatus with which it makes contact.

The next stage is the conversion of the ammonium diuranate to uranium tetrafluoride, a series of operations which is carried out in the "Dryway" plant. Trays containing the ammonium diuranate paste are stacked in a cylindrical reactor so that reactant gases which are introduced can pass from tray to tray across the surface of the contained solid. The reactor is lowered into an electric furnace, and the conversion proceeds in three stages. The diuranate is first heated to decompose it to uranium trioxide; during this calcination ammonia and steam are driven off. The trioxide is then reduced to dioxide by hydrogen, and finally the dioxide is treated with anhydrous hydrofluoric acid gas to convert it to uranium tetrafluoride. All these reactions are carried out in the same reactor which has a series of connections to the hydrogen and hydrofluoric acid supplies and to a caustic scrubber where effluent gases are either absorbed or discharged to atmosphere if harmless.

Reduction to Metal

The final step is the reduction of the tetrafluoride with metallic calcium. The uranium tetrafluoride is transported in drums to the reduction plant and calcium chips are added, the operations being carried out in an enclosed cabinet. The contents are mixed under an argon blanket by rumbling the drum and finally charged into the reduction mould. This consists of a mild steel casing resembling an inverted, truncated cone. It is lined with calcium fluoride which has been rammed round a wooden former and carefully dried. The mould is mounted on a bogey running on a light rail track which passes through a long drying oven, through a charging cubicle, into a firing chamber, and out again into a cooling bay.

The charged mould is moved forward into the firing chamber, and vertical, electrically operated doors lowered into position. The charge is fired by dropping into it an ignited pellet of potassium nitrate and lactose mixture. An elaborate system of inter-

locking controls ensures that the charge is only fired when observing full safety precautions.

The reaction in the mould is rapid and exothermic. The heat generated melts the uranium formed so that the metal runs down to the bottom of the mould where it forms a solid billet, while the calcium fluoride, which is the other product of the reaction, floats on top as a slag.

When the reaction is complete, the mould is moved forward by remote control into the cooling bay. After cooling, the mould is hoisted into a breakdown cubicle where it is inverted over a grid so that both the uranium billet and the calcium fluoride slag and mould lining fall out of the mould. The billet is finally cleaned and washed.

Recovery Stages

From all the wet processes effluent liquors arise and pass into a recovery section. To this section are also sent various solid residues from later stages in the process. The recovery of uranium from these effluents and residues forms an essential part of the whole process, and governs the over-all efficiency. The basis of all the recovery processes is to convert the uranium present in the material to uranyl nitrate, if not already present in that form. The uranium is then precipitated as uranium peroxide, and the recovered material rejoins the main stream at the ether purification stage.

Discussion and Future Possibilities

Despite the difficulties and the short time scale for design and construction, the plant has been wholly successful in operation. It started to operate on the programmed date and has from the outset achieved its designed output. This result has been quoted as a classic example of the proposition that, in appropriate circumstances, the elimination of pilot plant work can be accepted and may even be an advantage, since there is no possibility of the designer perpetuating inelegant features of a hastily built pilot plant.

The over-all utilization of uranium has been extremely good, despite the rather large recycles intrinsic in the process and the refractory nature of some of the slaggy reduction by-products. Since some of the effluents from the process as originally devised contained significant concentrations of uranium, precipitation recovery processes were introduced on the plant scale at an early date. These gave crude products which were stored originally but for which recovery processes are now available. Initially it was also necessary to store many of the solid residues, especially those of a slaggy nature where the uranium may be very finely dispersed or even in solid solution in the fluoride matrix. More recently, methods have been devised for recovering these residues, which are now being fed back into the main stream. This recovery process gives also a source of very pure calcium fluoride. The latter is now used for the reduction mould lining and has significantly reduced the impurity pick-up by the billet.

The health precautions have also been completely successful. There has been no case of radiation illness or of serious uranium poisoning.

Finally, the quality of the uranium metal produced has been entirely satisfactory for requirements to date. No difficulty has been experienced in the piles which can be attributed to the uranium metal production processes.

Nevertheless, in any new plant which might be built several fundamental changes might be considered. These might result either from new circumstances or from information obtained since 1946, such as:

(*a*) The necessary health precautions are better understood and could be implemented more economically by more refined design.

(*b*) The metallurgical condition of uranium for future reactors will probably have to be more closely controlled, requiring even purer metal.

(*c*) Future raw materials may tend to be uranium concentrates rather than virgin ores, but may come from a wide range of sources.

(*d*) Economies might be obtained by the introduction of continuous processes and cheaper reagents.

Economies in extraction will probably result automatically from the introduction of concentrates as feed and this change will also give greater flexibility in regard to the acid leaching conditions. Purification would clearly be cheapened by the substitution of a direct multi-stage counter-current solvent extraction process for the uranium peroxide and ether extraction stages. If successful, such a process would eliminate the use of expensive reagents such as hydrogen peroxide and would permit of much greater flexibility of decontamination whilst obtaining very high yields without tedious recycles.

From the pure uranyl nitrate stage an interesting possibility would be to carry out the gas-solid reactions of the "Dryway" process in fluidized beds. Further, it might be possible to produce uranium oxides by direct evaporation of uranyl nitrate and, again, a fluidized bed might be used. Many problems would need to be solved but, if successful, very high throughputs could be obtained from a small plant with very high reagent and uranium efficiencies.

For the reduction stages several possibilities exist, including methods of preparing uranium powders. If billets are required magnesium would obviously be a cheaper reductant than calcium. The Mg-UF_4 reaction does not provide so much heat as its calcium counterpart and side-reactions are more likely, especially if oxide refractories are used. A careful balance between scale of operation and method of heating would clearly be necessary to obtain complete reaction and good separation of metal and slag.

It is clear, therefore, that possibilities exist for improving the existing process and that if the ideas referred to could be developed successfully the production of uranium metal from concentrates would compare very favourably with the best practices for any other metal, with regard to cost, elegance of design and, especially, purity of product.

The Preparation of Pure Uranium Metal

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SUMMARY

A detailed description of the chemical processes employed for preparing pure uranium metal at the Bouchet Factory of the Commissariat à l'Energie Atomique (Seine-et-Oise), starting either with relatively high-grade ores, or with concentrates resulting from the physical or chemical treatment of low-grade ores. Nitric acid treatment of the ores leads to the production of impure sodium uranate. This in turn is dissolved in nitric acid, and the uranyl nitrate is extracted with tributyl phosphate diluted with an inert solvent. The pure re-extracted uranyl nitrate is successively converted into uranium peroxide, the orange oxide, and then the brown oxide, which is converted into the fluoride with anhydrous hydrofluoric acid. The uranous fluoride is reduced to metal by pure calcium, the yield exceeding 99%.

INTRODUCTION

The Bouchet Factory of the C.E.A. forms an enclave of about six hectares within the National Powder Factory of the same name, located in the department of Seine-et-Oise, near the small town of Ballancourt.

The first departments of the plant constructed in 1946/47, were fitted up for the purification of a limited stock of uranium oxide and sodium uranate, which was to furnish the pure oxide destined for the first pile of the C.E.A.

The development of the C.E.A.'s program and the discovery of important deposits of uranium ore, especially in the Massif Central, led to the progressive development of the Bouchet Factory which is at present equipped to produce ingots of nuclear pure uranium metal, starting with ore of different origin or with concentrates produced physically or chemically in the neighborhood of the mines.

Its productive capacity was figured out as a function of the general program of the C.E.A. and its actual production has been more than ample up to the present for all the activities contemplated within the framework of this program.

The Bouchet Factory is operated directly by the Commissariat à l'Energie Atomique and most of the processes in use there were developed by its technicians. On various occasions appeal has been made for the help of private industry, however, especially for the first refining installations (Société des Produits Chimiques des Terres Rares) and the present ore-dressing plant (Société Minerais et Métaux et Société de Potasse et Engrais Chimiques).

The ore can be converted into the pure metal in three steps:

The first is intrinsically variable with the ore, and consists of extracting the uranium and converting it into crude sodium uranate.

During the second step, the crude uranate is converted into nuclear pure oxide.

The third stage is the conversion of the oxide to the metal by way of the fluoride.

PREPARATION OF SODIUM URANATE STARTING FROM THE ORE

The ore-dressing varies, depending essentially on the origin, nature, and concentration of the raw materials. The principal products at present treated at Bouchet are ores from La Crouzille (Hte-Vienne) and from the Bois Noirs (Loire) the principal constituent being pitchblende, or flotation concentrates from Lachaux (Puy-de-Dome) and Margnac (Hte-Vienne) where two physical concentration mills are installed which treat chiefly ores containing double phosphates of uranium.

The products are relatively rich, and it is essential to extract the uranium from them with a high yield which can generally be performed by means of nitric acid digestion at about 60° C.

The following flowesheet is common to all these ores and concentrates with variations for each particular case.

The ores—titanates or niobotantalates—are digested with concentrated nitric acid at the boiling point. This category includes a rather large quantity of ore from Mozambique, which the C.E.A. was able to buy by the kind authorization of the Portuguese Government.

In every case the digesting solution (which contains all the uranium of the ore) is decanted in stainless steel Door Oliver thickeners. The residues are thoroughly washed.

The solution is then treated with sodium carbonate, which precipitates such metals as iron, manganese, lead, etc., in the form of hydroxides, bicarbonates, or phosphates, leaving the uranium in solution in the form of uranyl carbonate.

The precipitate is washed on filter presses and forms a manufacturing residue, while the filtrate is treated at the boiling point with a solution of

Original language: French.

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caustic soda, which precipitates sodium uranate practically quantitatively.

In addition to this nitric acid procedure, which is the most practicable and the most universal, the plant is likewise equipped for sulfuric acid digestion, which is better suited for certain types of ore and is always more economical.

Some other procedures, such as direct digestion with sodium carbonate, or a process involving precipitation of uranium phosphate from solutions produced by sulfuric acid digestion of low-grade ore, have been studied by the C.E.A. or in collaboration with outside organizations beyond the Bouchet plant.

Obviously, the most generally used treatments in the Bouchet plant have many variants, and a suitable and economical treatment had to be sought for each new type of ore.

This has made it possible to treat flotation concentrates containing a considerable amount of organic reagents under very satisfactory conditions. When a large quantity of lead is present, it is precipitated during digestion. Sometimes the dressing of different types of ore is combined in order to eliminate drawbacks that are encountered when they are dressed separately. In every case, the aim is total solubilization of the uranium with the lowest expenditure of reagents and the formation of easily filterable products. The recovery of certain impurities such as lead, titanium and zirconium has been explored but not put into practice.

It should be noted that radium is no longer recovered in these operations, but that care is taken during digestion, to make it insoluble by the addition of barium carbonate, and, if necessary, sulfate ions to keep the radium-barium sulfates insoluble in the sterilizers and make them unable to pollute the rivers into which the waste water might be diverted.

The chemical plant in which the treatments described above take place is preceded by an ore-reception plant where it is dried, ground, sampled, weighed and stored.

The equipment also makes it possible to build up relatively large lots of constant composition.

In the case of ores that are received moist and finely divided, dry storage is replaced by a hydraulic return plant.

The over-all yield of the physical and chemical operations in these departments is in the neighborhood of 97%, the initial content of the ores treated varying from 2 to 10% and even more.

Treatment of ores assaying less than 2% of uranium has been left to mills in the neighborhood of the actual mines.

PURIFICATION OF URANIUM COMPOUNDS

The purification of the sodium uranate obtained from the various ores is based on the property of uranyl nitrate of being soluble in organic solvents, a property that it has in common with the nitrates of elements of the periodic table from thorium on.

In recent years methylisobutyl ketone (hexone) has been used for this extraction at the Bouchet plant, using ammonium nitrate as a salting-out agent; the presence of this salt in the aqueous solution displaces the equilibrium of the uranyl nitrate, which is dissociated into ions, toward the molecule, which alone is soluble in the solvent. For the last few months hexone has been replaced by tributyl phosphate, the use of which makes a salting-out agent unnecessary.

It may be mentioned that ether was the first solvent employed at the Bouchet plant for the extractions of uranyl nitrate, but it was abondoned rather soon for reasons of economy and safety.

Tributyl phosphate, although rather expensive, does not entail any high costs, since it can be almost entirely recovered. Moreover, in use it is diluted with one and a half volumes of a hydrocarbon, which is not an expensive substance.

Countercurrent extraction is effected in two stainless-steel columns five meters high, packed with Rashing rings. While nitrates of all the ordinary metals remain in aqueous solution, the solvent leaves by the top of the column, carrying all the uranyl nitrate with it. In practice, a small percentage of uranium rests in the bottom and is recovered in a separate operation.

The next operation consists of re-extracting the uranyl nitrate with distilled water in a countercurrent column five meters high. The dispersion of the phases was specially studied in order to obtain perfect re-extraction in a single passage.

All these solutions contained free acid in a quantity sufficient to prevent any precipitation during these operations.

The result at this point is that almost all the impurities have been eliminated, but the uranium is in a dilute solution as the nitrate. Precipitation of uranium as the peroxide was chosen for passing to the solid phase, since this makes it possible to eliminate at the same time the few impurities still remaining.

The uranium content of the solution during these various operations is as follows: crude aqueous solution to be extracted, 370 gm U/liter; solution of uranyl nitrate in the solvent, 140 gm U/liter; solution of pure nitrate in distilled water, 70 gm U/liter.

The work is done in heated tanks with stirring, adding oxygenated water and ammonia to the uranyl nitrate; the ammonia is intended to hold the solution pH at a fixed value throughout the precipitation.

This operation is followed by filtering and washing the peroxide, which has been freed of its last impurities which remain in the mother liquor whose pH is about 1.5. However, there still remains a little iron, manganese, silica and some other common impurities, which total only a few parts per million compared to the uranium. Such elements as boron, lithium, cadmium, and the rare earths, which are veritable poisons for atomic energy, are practically undetectable in the pure oxide. Here is an analysis of the impurities found in the pure oxide of the usual grade (in ppm): Fe 1.5, Mn 0.3, Ni 0.2, Cr 0.4, Cd 0.2, Cu 0.3, and Mo 0.3.

REDUCTION OF THE PURE OXIDE AND PREPARATION OF THE METALLIC URANIUM

Ingots of metallic uranium have been produced on an industrial scale at the Bouchet plant ever since 1950, following a technique developed and perfected by the Bouchet team.

Although the purity of the final product, which was already satisfactory by then, has not changed much, the procedure employed has undergone many changes and improvements since that time.

The various stages of manufacture for converting the peroxide into metallic uranium are as follows: (*a*) transformation of UO_4 to UO_3 by simple heating to about 400°; (*b*) conversion of UO_3 to UO_2 by reduction with ammonia gas in a continuous vertical furnace; (*c*) preparation of tablets of the UO_2 oxide for fluorination; (*d*) conversion of the UO_2 tablet to the fluoride by the action of anhydrous hydrofluoric acid gas in a continuous vertical furnace; and (*e*) reduction of the uranium fluoride by pure calcium, to the state of molten uranium which forms ingots upon cooling.

Since the materials, the products, and the reagents employed in these last transformations should introduce only a minimum of impurities into the uranium, working out the procedures required solution of a number of auxiliary problems; these problems were sometimes solved with private industry.

Thus, preparation of the calcium of nuclear purity was entrusted to the Société Métallurgique du Planet, which specializes in the manufacture of light metals. At present this company is furnishing double-distilled calcium.

The procedure initially used is a classic alumino-therm one according to the equation:

$$3CaO + 2Al = 3Ca + Al_2O_3$$

This is done in vacuo at about 1300° in refractory cement furnaces, the charge being heated by direct radiation, using graphite resistors.

The crude calcium is purified by sublimation in a retort at a very high vacuum. It is then absolutely pure from the nuclear point of view. The only impurity present in any considerable amount (0.1%) is magnesium; no attempt was made to eliminate this, since it plays the same reducing role as calcium in reducing the uranium fluoride. The total of all the other foreign bodies is not more than a few tenths of a part per million.

The calcium is recovered in the form of cakes 40 cm in diameter, weighing about 14 kg. They are used in the form of turnings.

Another auxiliary problem was perfecting the special technique that makes it possible to prepare crucibles of pure calcium fluoride, starting with the purified natural fluoride coming from the factory of the Société Teisset-Kessler, at Clermont-Ferrand.

These crucibles can take the molten uranium without deformation. They are manufactured in a shop that is a part of the factory. The calcium fluoride, which must have a physical structure making it suitable for this use, does not contain more than 0.5% of foreign elements (especially Fe and Si).

Here are some technical details of the reduction process proper:

1. There is no special problem in the transformation of UO_4 to UO_3, which is effected either in special large vats or in a tunnel furnace.

2. The reduction of the UO_3 in a vertical furnace was initially performed by a current of hydrogen at 750°. The gas was diluted with an excess of nitrogen to make it easier to control the exothermic reaction. Later we used a mixture of hydrogen and nitrogen produced by cracking ammonia; we now reduce it directly by a current of ammonia, this gas breaking down into its elements as soon as it comes into contact with the uranium oxide. Since the action of the nascent hydrogen has a very favorable influence on the yield of the apparatus, it is possible to reduce more than 1000 kg of oxide in twenty-four hours of operation in a vertical furnace about one meter long, followed by a cooler of the same dimensions.

The UO_3-UO_2 reduction furnaces operate automatically, the gas flows being measured and regulated by rotameters, and the final product which is slightly oxidizable, being maintained in an inert atmosphere.

3. The fluorination process used for five years at the Bouchet plant converted the UO_2 by attacking it with a 40% solution of pure HF.

Digestion is done in a tank lined with ebonite and with an agitator also covered in ebonite. A single operation involved 100 kg of UO_2 and an excess of HF of about 25% over the theoretical quantity. The oxide is introduced portion-wise with stirring, in order to prevent the mixture from heating up to above 60°. After the end of the reaction, the mixture is filtered in an ebonite-covered filter using a polyvinyl chloride cloth, washed with water and added HF, and finally washed with methanol.

Drying of the fluoride requires great care, for humidity is responsible for spattering during processing, causing a considerable decrease in the yield and the quality of the metal. On the other hand, desiccation lasting too long a time or at an excessive air temperature results in serious hydrolysis and oxidation of the fluoride.

The air-dried cake, containing about 50% moisture, is subjected to a preliminary drying at 200° in a lead-lined tank. The product then contains 2–3% of water; it is broken up in a crusher fitted with uranium jaws (to prevent the introduction of fresh impurities) and redried at 500° in a vertical copper oven in an atmosphere of hydrogen, with or without HF added. The moisture content upon emerging from this oven is not more than 0.3%, as determined by loss of weight in vacuo at 150°. It does not contain any higher uranium oxides and a very low percentage of uranous oxyfluoride. The increase in humidity during storage is negligible.

The *anhydrous fluorination* process used at present in the Bouchet plant is very similar to the UO_3-UO_2

reduction in a vertical furnace, as far as apparatus is concerned. It was adopted after experimenting with many possible variations of fluorination by the anhydrous gas. Of the continuous processes, fluidization, horizontal furnaces, and vertical furnaces with trays have yielded fairly satisfactory results.

Use of the present vertical furnace (without trays) was made possible by the preliminary agglomeration of the uranium oxide into pellets, preventing the swelling of the substance and making automatic regulation fairly simple.

The furnace, the apparatus, and the auxiliary circuits were constructed of special corrosion-resistant materials, such as: monel metal, copper, graphite, plastics; the corrosion problems varying from one point to another.

The furnace consists of a vertical tube flaring slightly toward the bottom, situated in an electric furnace which is only used at the outset as the reaction is sufficiently exothermic to continue thereafter without supplying any heat.

The temperature in the hot zone is held at about 450–500°.

The gas used may contain a certain amount of nitrogen or even of hydrogen and it always contains at least a 20% excess of hydrogen fluoride over the theoretical amount.

The fluoride produced may contain from 1 to 1.2% of oxygen without this affecting subsequent operations as the fluoride is always completely reduced to the metallic state.

Improved techniques made it possible to produce ingots of the pure metal on an industrial scale as early as 1950 but further improvements are being constantly made in order to make this operation simpler and cheaper.

The crucibles now in service make it possible to produce one ingot per crucible per day (the ingot may weigh as much as 100 kg). The yield of the operation is as high as 99%, and the quality of the metal obtained is such that rods can be prepared for the piles by direct drawing or melting.

The crucible has an outer shell of stainless steel and is completely lined with calcium fluoride to prevent any contact that might contaminate the metal.

After the crucible has been filled with a mixture of UF_4 tablets and calcium chips, it is covered with a steel bell cover. It is then evacuated and then filled with pure argon gas. At the moment of starting (which is done electrically), a valve is opened to allow the escape of the excess calcium which oxidizes immediately in the air. After the reaction, which lasts only a few seconds, the bell is closed again and the ingot is cooled in an argon atmosphere by a jacket with circulating water.

The ingot, topped by a mass of molten fluoride, is removed from the oven by a special device.

This brief sketch of the chemical transformations involved in the uranium cycle gives a picture of this industry which has been recently created in France thanks to the close and indispensable technical collaboration of private industry. The C.E.A. devotes more than a third of its annual appropriation to the search and mining of uranium ores and the production of the pure metal; efforts are constantly being made to lower the cost of production by effecting improvements and changes at each point in the chemical cycle.

Uranium Metallurgy in Belgium

INTRODUCTION

The special interest which became apparent in the scientific and industrial circles of Belgium since the last world war, with respect to the development of nuclear science and its industrial application, was obviously to be expected in view of the important position which the Belgian Congo, and particularly l'Union Minière du Haut-Katanga, occupies in the production of uranium.

In 1951, the King appointed a Commissioner in charge of Atomic Energy, in the person of Mr. Pierre Rijckmans, Honorary General Governor of Belgian Congo, a decision which was going to be the starting point for a series of moves which were to give organic form to the initiatives of the academic and industrial circles.

The first, under the auspices of the National Scientific Research Foundation, was the creation of an *Institut Interuniversitaire de physique nucléaire*, which would henceforth guarantee stability and continuity, and provide means of action for the research undertaken in our universities.

In 1952, the Atomic Energy Commissioner created the *Centre d'Etudes pour les applications de l'Energie nucléaire*, the activity of which was to be directed by qualified representatives of the administration, scientific circles and industry. This Center decided on building the first Belgian experimental nuclear reactor at Mol, as well as chemical, physical, electronic, metallurgical and technological laboratories. The Mol facilities must permit Belgian science and industry to get their initiation into the problems raised by the application of atomic energy, and to help in training personnel which will be responsible for the building and operation of power reactors.

In 1954, the electricity producing societies formed the *Syndicat d'Etudes de Centrales Atomiques*, the purpose of which is to study all aspects of the utilization of nuclear power reactors within the framework of the production of electrical energy in Belgium.

The main industrial companies in the country, on their side, created the *Syndicat d'Etude de l'Energie Nucléaire*, the purpose of which is to conduct research into the building and operation of nuclear power reactors in Belgium and abroad.

The last two named organizations decided to study and carry out by their own means, and for the near future, the building of a nuclear plant in Belgium, and to exploit it industrially.

The decision taken by our industrialists to play an active role in the future equipment of our country and others with nuclear power plant rests on the assurance of an adequate supply of nuclear fuel, particularly of uranium.

The Société Générale Métallurgique of Hoboken, a subsidiary of the Union Minière du Haut-Katanga, is known for it important role in the production of uranium. Before the world war, it was interested in the making of uranium and ferro-uranium salts. Since then it has concentrated on the production of uranium, as well as of thorium of nuclear purity.

It has just decided on setting up a facility for the industrial production of natural uranium.

The plant will start operations in 1956, and the purpose of this paper is to give an brief description of the methods which will be used for the purpose.

DESCRIPTION OF THE PROCESSING OF METALLIC URANIUM

The raw material is a uranium bearing concentrate, which contains more than 80% U_3O_8, supplied by the Union Minière du Haut-Katanga. The impurities contained in the concentrate will be listed in decreasing order of their contents: MgO, SiO_2, Pb, CaO, P_2O_5, Cu, Mo, Co + Ni.

The production of metallic uranium from the concentrate is a two-stage operation: chemical treatment, meant to produce a nuclear purity oxide $UO_4 \cdot 2aq$; and metallurgical treatment, for the subsequent transformation of the oxides, fluorination and reduction to metal.

CHEMICAL TREATMENT

Dissolving the Concentrate with Nitric Acid

The purpose of this is to obtain a clear and sufficiently concentrated solution of uranyl nitrate from which uranium can be extracted nearly quantitatively by means of an organic solvent (for instance methylisobutylketone, ether, etc.).

To this end, the concentrate is attacked by nitric acid, an operation followed by a separation (filtration) of the insoluble residue.

A given quantity of salting agent is added to the clear solution (in our case recycled magnesium nitrate). The function of the salting agent, as is well known, is to make the passage of the uranyl nitrate to the organic phase easier and thus to increase markedly the efficiency of the extraction process.

The clear uranyl nitrate solution has a density of ca 1.5 and an U_3O_8 content of ca 225 gm/l.

The residue from the reaction, dry, represents approximately 1% by weight of the charged con-

Original language: French.

centrate and its U_3O_8 content is less than 1%, namely less than 0.01% of the uranium added. This residue is set aside.

Attack is carried out with concentrated nitric acid. The uranium containing concentrate is brought dry to the reaction vat, following which a quantity of concentrated nitric acid of technical quality ($d = 1.4$) required for dissolution is added. The reaction is very exothermal, and the temperature of the mixture may reach approximately 100°C.

The mixture is heated and kept at a boil (120 to 130°C) for approximately one hour. A black foamy mass rises to the surface at the beginning and becomes progressively transformed into gelatinous particles which diffuse through the boiling solution and deposit when the heating is stopped. Thereafter, dilution is made with a part of the recycled magnesium nitrate solutions (salting agent). The solution is filtered. The filtration gives very satisfactory results. The gelatinous insoluble product—which is very dense—is removed from further processing.

Uranium bearing solutions from the washings are added to the clear solution. Thereafter, the missing quantity of recycled solutions of magnesium nitrate is added, and, if the density of the solution is still too high; it is diluted with water until a density of approximately 1.5 is reached.

Extraction of Nuclear Purity Uranyl Nitrate

The aqueous solution of uranyl nitrate obtained from these operations must be purified, from the impurities which have been introduced during the dissolving operation. This purification rests on the well known property of some organic solvents of dissolving uranyl nitrate preferentially to most other metallic nitrates.

The operation is conducted in three stages:

Primary Extraction

Primary extraction is the first and most important phase of purification. The separation of uranium and metallic impurities is carried out by means of ketones. Several ketones have been considered. Although the results of extraction were, as a rule, satisfactory, economic reasons have mostly dominated the choice.

A method of extraction by ether was also developed—as a matter of fact with success—but it was abandoned, mostly due to the danger inherent to the use of large amounts of ether.

Extraction is carried out in a centrifuge type apparatus, entirely closed, having three theoretical extraction stages operating countercurrent and with all the parts which come into contact with liquids being made of stainless steel. Each stage includes: a mixer, for the intimate mixture of the two phases; and a high speed centrifuge, for separating the phases.

Feed is by gravity, the solution tanks being under positive pressure with respect to the rest of the equipment. Turbines are used to establish the pressure, without creating any foam, to a load of 1.5 kg/cm², which makes it possible to feed these liquids to the tanks.

The characteristics of our methods of procedure are the following:

The ketone/uraniferous solution ratio at extraction is 1.5/1. The outputs may reach about 500 l/hr on the solution side and 750 l/hr on the methylisobutylketone side.

It is of advantage to operate at a low acidity in order to rule out such hydrolyses as would interfere with successful operation.

The extraction efficiency of uranyl nitrate exceeds 99.5%. Indeed, the depleted solution contains less than 0.5% of the uranium used, as well as nearly the whole of the impurities and salting agent ($Mg(NO_3)_2$).

In a recovery operation, the uranium which is not extracted is precipitated with most of the impurities. Following filtration, it is set aside for subsequent treatment. The salting agent which remains in solution is used again at the beginning of the cycle when the solution is made up.

Wash

The ketonic solution of uranyl nitrate still contains traces of impurities.

In order to complete purification, the ketone phase is washed either with a small amount of a saturated aqueous solution of pure uranyl nitrate or with a small amount of demineralized water.

The impurities leave the ketone phase to enter the aqueous solution, until equilibrium is established as imposed by the distribution between the two liquid phases. It is obvious that uranium also distributes between the two phases:

1. One part is in the impure aqueous solution; it depends on the amount of washed solution used. This uranium is recycled, and reintroduced at the beginning of the solution system.

2. Another and much larger portion remains in solution in the ketone; this is pure uranium, to be reextracted.

The quantities of solution involved depend on the wash water/ketone ratio. We usually have a ratio of some 1/10.

Washing is carried out in a stainless steel column equipped with a stainless steel filler, in order to make for closer contact between the phases, and to increase the efficiency of the wash.

At the end of the wash, the ketone solution of pure uranium contains approximately 83% of the whole of the uranium; the impure wash solution contains about 17%. This solution, as already stated, is recycled and brought in again at the beginning of the extraction process.

From the standpoint of purification, the washing operation is efficient and affects all the impurities still present, including vanadium and the rare earths; this as distinct from the subsequent peroxide operation, which, under our conditions, does not completely eliminate these elements.

According to the composition of the concentrates to be treated, it is thus possible to leave out this operation, if subsequent peroxide treatment is of adequate efficiency.

Reextraction

The purpose of reextraction is that of passing the uranyl nitrate from the washed ketone solution into an aqueous phase made up of very pure demineralized water, and to recover the ketones, which are used again for primary extraction. This operation is carried out in equipment which is in every way identical to that used for primary extraction.

The reextraction ratio: uranium containing ketone/demineralized water, is approximately 1/0.75.

Separation of the phases from the reextraction is difficult and may result in some entrainment in the extractor, particularly at a high output.

Preheating of the solutions (ketone and water) and slight acidification of the water make it possible to accelerate phase separation and to reach, without any difficulties, the high outputs required in order to be able to treat the solutions from the primary extraction in the wash.

The solvent loss is less than 5% for a complete cycle: extraction—wash—reextraction. This is due to the fact that the aqueous solutions, during purification, are saturated with ketone, the recovery of which is not economical.

On the other hand when extraction is by ether, recovery of the solvent which saturates the aqueous solution is necessary, both for economic reasons (the losses are too great), and for safety reasons (processing saturated ether solutions is dangerous).

Precipitation of Uranium Peroxide n.p.

Peroxide treatment consists of precipitating the uranium peroxide of a slightly acid solution of uranyl nitrate according to the reaction:

$$UO_2(NO_3)_2 \text{ (in aqueous solution)} + H_2O_2 \rightleftarrows UO_4 \cdot 2H_2O + 2HNO_3$$

With this process, the last impurities which might have escaped extraction in the wash, are held in solution. In addition, uranium peroxide is readily reduced to a lower valency oxide. Thus, it is a good starting product for metallurgical operations.

As indicated by the literature, precipitation generally is carried out in the following fashion:

To the slightly acid hot solution ($> 40°C$) of uranyl nitrate, the required quantity of perhydrol is added slowly (use up to twice the theoretically needed amount) with energetic stirring.

In certain operating techniques, an ammonia solution (or gaseous ammonia) is added at the same time as the perhydrol in order to neutralize the nitric acid formed by the reaction itself.

Thus, the pH of the solution is kept constant throughout the duration of precipitation which favors subsequent filtration and the yield of precipitation.

In order to achieve precipitation giving a precipitate which can be filtered without any undue difficulties, several factors must be borne in mind at all times: concentration, acidity, temperature, stirring, duration of operation, etc.

The optimal conditions, as generally recommended are: concentration of uranyl nitrate solution, 5 to 10%; acidity, pH between 1 and 3; temperature over 40°C; vigorous stirring.

Our experience shows that this is an essential operation, if, in the subsequent treatment of the oxide and during fluorination, products of consistent composition and high efficiencies are desired.

Each of the characteristics of the precipitation was the object of a systematic study, for the purpose of achieving a fine crystalline precipitate of sufficient weight which would settle immediately after agitation is stopped, a rapid filtration not slowed down by the thickening of the cake, and an effective wash.

The cake obtained on the vacuum filter contains 40% moisture. The precipitation yield exceeds 99.9%.

The quantity of perhydrol used is less than double that needed theoretically.

The traces of uranium contained in the filtrate are precipitated with magnesium and separated by filtration, and charged again with concentrate at the beginning of the cycle.

The chemical treatment facilities have been so installed as to make the operation fully automatic and to guarantee complete security against fire and explosion.

METALLURGICAL TREATMENT

The peroxide $UO_4 \cdot 2aq$ produced by chemical treatment is transferred to the metallurgy department, where the treatment consists of four stages: drying of the peroxide, calcination which transforms it into UO_3 and reduction to UO_2 by hydrogen; fluorination of UO_2 to UF_4; reduction of UF_4 to metallic U by calcium; and vacuum melting of the first uranium obtained.

Drying, Calcination and Reduction

The three operations are carried out successively in the same type of vertical oven (bell oven) using a batch process, similar to those used in powder metallurgy. The heating bell is fixed on the top of the container in which capsules which contain the product to be treated are piled up.

Drying and Calcination of the Peroxide

The wet peroxide (30 to 40% water) is placed in the oven at 450–550°C, at which temperature drying and calcination are very rapid.

At the beginning, the free moisture evaporates, while the temperature in the centre of the charge keeps at about 100°C. Once the major part of the free water is evaporated, the temperature of the charge begins to rise: the 2 molecules of the water of hydration begin to separate at the same time as a part of the oxygen, since UO_4 is not very stable in its anhydrous form. At the end of calcination, the

atmosphere in the oven is made up of nearly pure oxygen, and of a very small amount of steam.

It is felt that calcination is terminated once the temperature in the mass of the charge reaches 350°C.

UO_3 produced by calcination is reddish in the zones where the temperature remained in the vicinity of 350°C, and a dark greenish-brown in the zones where the temperature was much higher.

This characteristic coloring makes it possible to make a distinction between the products which, following reduction, will give a slightly pyrophoric UO_2 which is friable and contains no hard grains. When UO_3 is orange or of a lighter greenish-brown, it contains hard grains (sintering) and gives, following reduction, a substantially more pyrophoric UO_2 which also contains hard grains. Sintering and pyrophorism of the final UO_2 depends mostly on the nature of the peroxide from which one starts, namely on the conditions under which this peroxide was obtained at the commencement of the chemical treatment.

Reduction

The oven which contains the calcinated product is then scavenged with nitrogen before the hydrogen needed for reduction is introduced.

Reduction can be carried out over a wide temperature range. We worked between 500 and 600°C, where the reaction is rapid and complete.

The rate of the reaction is not very sensitive to the composition of the gas mixture, when working with hydrogen and nitrogen.

It is possible to work with relatively thick charges, but several considerations led us to reduce the thickness of it to a few centimeters.

Where UO_2 must be taken out of the oven following reduction, the oven is charged with CO_2 after complete cooling off. This makes it possible to avoid the firing of slightly pyrophoric charges of UO_2. When the UO_2 is truly pyrophoric, this precaution is insufficient to avoid reoxidation of UO_2 during the unloading of the oven.

Pyrophoric UO_2 is particularly unsuited for the techniques where UO_2 is exposed to air, before it is subjected to fluorination.

Fluorination of UO_2 to UF_4

In our pilot plant, fluorination was carried out according to two different methods, the industrial conditions of which we studied with great care, namely: indirect ammonium hydrogen fluoride fluorination, and direct fluorination by anhydrous hydrofluoric acid gas.

We shall give a short description of each of the methods.

Indirect Fluorination with Ammonium Hydrogen Fluoride

The method has its origin in the work of Professor Decroly and his group, at Brussels University. It has been adequately described in the patents and in the literature. Therefore, we shall but briefly list its characteristics.

It is characterized by the use of ammonium hydrogen fluoride (NH_4HF_2) as a fluorinating agent. Uranium dioxide UO_2 also is transformed into a double fluoride of uranium and ammonium. The double fluoride then is decomposed under vacuum to uranium tetrafluoride UF_4, and to a neutral fluoride which is retransformed into an acid fluoride of ammonia which can be recycled.

Preparation of the Double Fluoride

The finely crushed ammonium hydrogen fluoride is intimately mixed with UO_2 in the mixing drum. The mixture is charged in small containers and heated in a vertical fluorination oven, at a temperature higher than the melting point (125°C) of ammonium hydrogen fluoride.

Besides the steam and ammonia liberated by the reaction, a part of the bifluoride also is evaporated.

Decomposition of the Bifluoride

Once fluorination is terminated, the charge which consists essentially of slightly wet double fluoride, is tranported to the decomposition oven. This oven is equipped with a vacuum pump capable of establishing a vacuum of a few microns. The heating curve is adjusted according to the pressure inside the oven; this pressure also makes it possible to determine when the operation ends.

When heating, it is necessary to allow for the release of steam which causes partial hydrolysis of UF_4 at the surface of the charge.

The product obtained is powdery and can readily be unloaded; no difficulty is encountered during the reduction with calcium, since its nitrogen content is less than 15 ppm, and humidity under 0.2%.

Direct Fluorination by Anhydrous Hydrofluoric Acid Gas

Direct fluorination is simpler than the bifluoride technique, since the UO_2 is transformed directly to UF_4 by hydrofluoric acid gas according to the reaction:

$$UO_2 + 4HF \rightarrow UF_4 + 2H_2O$$

Although anhydrous hydrofluoric acid gas is a very corrosive and dangerous reagent, it can be stated that an installation which operates with hydrofluoric acid is not much more dangerous that one using another fluorination reagent, once the techniques have been mastered which make the completely safe handling of the reagent possible.

The four operations: drying, calcination, reduction and fluorination, are carried out in the same type of vertical oven (bell oven), the container of which is filled with special pellets carrying the charge.

In the course of drying and calcination, there is no communication between the containers, the steam and oxygen are evacuated to the outside.

Reduction and fluorination are conducted in the following manner: several containers are connected

in series, in order to obtain a utilization of the hydrogen and hydrofluoric acid as complete as possible. During fluorination, anhydrous hydrofluoric acid is let in the first container, the charge of which is to be completely fluorinated; the others are used to recover the hydrofluoric acid.

The working temperature of the various ovens depends on the position of the container in the gas circuit.

When fluorination is accomplished in the first container, the hydrofluoric acid is let into the next, while a new container, which contains freshly reduced UO_2, is placed at the end of the hydrofluoric acid circuit.

Following fluorination, the containers are opened and unloaded in a separate well ventilated hall, where all precautions have been taken to guarantee personnel safety.

Reduction of Uranium Tetrafluoride by Calcium

The uranium tetrafluoride which we obtained in the stage just described, is always finely powdered, and requires no preliminary crushing before calcio-thermal reduction.

The calcium utilized as a reducing agent is in the form of fine chips.

This reagent must be very pure. The presence of nitrogen and magnesium accounts for the sometimes violent course of the reaction. On the other hand, if calcium contains manganese, this will pass into the uranium, which is inconvenient, since its capture cross section for slow neutrons is very high.

The uranium tetrafluoride is in the form of a fine dust and it is mixed with calcium under a hood. The loading of the reactor and calcio-thermal operation are also carried out under a fume removing hood. The workers carry special clothes and masks, in order to protect them against the dust.

The reduction of uranium tetrafluoride is carried out in the open air, in a reactor which has been covered with suitably tamped powdered fluorite. The collecting crucible is at the bottom of the reactor, in which the metal gathers as it separates from slag.

The crucibles are pressed vessels, sintered at 850°C for 20 minutes. Some techniques also have been developed to make crucibles and sintered fluorite vessels without pressing. The mixture of uranium tetrafluoride and calcium chips, which contain approximately a 20% excess of the reducing agent, is placed in the reactor in such a way that the two constituents of the charge do no segregate. When the weight of the ingots to be cast is fairly low (about 20 kg for example), it is appropriate to add a small amount of iodine to the part of the charge which is in the collecting crucible, at the bottom of the reactor. The purpose of this added iodine is to improve locally the fluidity of the slag at the beginning of the reaction, and to increase the amount of heat released in the small amount of charge which is in the crucible. The use of iodine is not necessary when the ingots are bigger (over 40 kg).

The reaction is started by a mixture of magnesium and sodium peroxide chips. This inflammable mixture is lit with magnesium tape, started with a torch. Remote devices can be used for large charges.

Since the humidity of the tetrafluoride is less than 0.15% and the reactor is vacuum dried before operation, there is very little sputtering. The few projections at the beginning of the reaction are due to the inflammable mixture.

The reaction is rapid and lively.

Once the reaction is finished, the reactor is closed, and evacuated and the argon admitted, so that the metal can cool off in the absence of oxygen, nitrogen and atmospheric humidity.

Cooling is very slow. Once that is finished, the impurities above the uranium ingots, in the crucible, are taken out.

After taking out of the oven, the ingots are carefully washed and cleaned.

A sample is taken from each ingot and sent to the laboratory for estimation of the impurities.

The uranium yield from the calcium reduction is close to 98%, and improves as the weight of the ingots increases.

The impurities consist of two layers; a greenish brown upper one, very poor in uranium which contains a few hundredths of one per cent of uranium; and a lower part, which is dark, much richer, and contains up to 10% of uranium. These are difficult to separate. They are sent back for chemical processing, and recovery of the uranium.

Vacuum Melting of the First Uranium Produced

This operation permits the elimination at least in part, of some impurities such as hydrogen, oxygen and nitrogen. Hydrogen and nitrogen have an absorption cross section for thermal neutrons which is fairly large; on the other hand, hydrogen has brought about the breaking of the cladding in some nuclear reactors. Vacuum casting also permits: (1) the elimination of traces of impurities carried into the metal during the calcio-thermal reduction; (2) the casting of rods which, following machining and cladding, can be used in nuclear reactors; (3) the casting of ingots which, from the outset, have the dimensions required for rolling, forging, extrusion or die casting.

Fusion is carried out in a graphite crucible or alumina crucible, extended by a graphite sleeve, the purpose of which is to avoid a break in the alumina crucible by thermal shock. The alumina crucible is surrounded by a graphite one: it does not enter into direct contact with the latter, but is separated from it by a thin sheet of molybdenum. Thus, reduction of the alumina by the graphite in vacuum is avoided, a reaction which releases CO and may thus create oxidation of the melted uranium, and formation of carbide in it.

The moulds are made, either of graphite or steel (ordinary steel or preferably stainless steel). The surface of the moulds is polished or equipped with a "mould dressing."

Heating is by induction, the frequency used being such that an important fraction of the heat is developed direct in the metal, and that the turbulence created in the mass of the melted metal makes degassing easier.

The bath is purified before casting. This is done by tilting the induction coil which carries the crucible, but it can also be done by means of a plug at the bottom of the crucible (bottom-pouring).

The ingots thus obtained are sent to another department for subsequent mechanical transformation of the metal to the dimensions required by the nuclear reactors for which they will be used. Description of the mechanical transformation operations is not included as it does not fall within the scope of this paper.

CONCLUSIONS

Belgium will soon have an industrial installation for the production of nuclear purity natural uranium. The processing techniques to be applied are inspired by those generally used in other producing countries.

The merit of our technicians is that, in the absence of reliable information on the subject matter, they developed and applied methods, some of which probably are original.

The high assay of the raw material with which we begin, the operating techniques, the high degree of automation and the capacity of the installation warrant the statement that the cost will be competitive. We hope it will be an important contribution to the efforts aiming at the utilization of nuclear energy.

The Preparation of Uranium Metal by the Reduction of Uranium Tetrafluoride with Magnesium

By H. A. Wilhelm,* USA

This article is based on experiments, studies and observations made in connection with the development and operation of a large-scale low-cost process for the production of high purity uranium metal. The work leading to this process was begun early in 1942 by scientists at Iowa State College as a part of the pressing atomic energy effort of the nation at that time. Details relative to the resulting process and certain special purpose variations are presented.

A survey of the available literature in 1942 revealed that uranium metal could be prepared by any one of a number of methods. Laboratory tests on some of the more promising of these methods for production were subsequently reproduced. These tests showed, however, that the methods described in the literature either gave poor quality uranium metal or left much to be desired processwise for a large-scale low-cost operation. These conditions warranted an exploratory effort directed toward the development of new methods for the preparation of uranium metal. A process employing the reduction of uranium tetrafluoride with calcium was our first major step in the desired direction. This process was soon followed by the development of the method for producing uranium metal from uranium tetrafluoride with magnesium.

When the program on atomic energy in the USA was expanded early in 1942, there were two producers of uranium metal operating on a small scale in America. One producer used calcium hydride for the reduction of uranium oxide. The mixture of UO_2 and CaH_2 was placed in a steel cylinder inside a retort which was heated to 960°C. After the reaction occurred, the charge was allowed to cool under a vacuum to eliminate the hydrogen. The product of the primary reaction was a sintered clinker, which which was then crushed to a powder. This powder was subsequently leached with dilute acetic acid, washed, dried, briquetted and sintered to form a fairly dense metal. This uranium was rather impure and contained considerable oxide.

The other producer employed an electrolytic process in which either KUF_5 or UF_4 was dissolved in a fused salt mixture of 80% $CaCl_2$ and 20% NaCl in a graphite crucible. This crucible served as the anode and the uranium was electrolyzed out in the form of a granular deposit on a central molybdenum cathode. A temperature of about 900°C was employed for the fused salt electrolyte in order to produce coarser, less pyrophoric metal. The uranium was subsequently leached, dried, briquetted and melted and cast in beryllia crucibles to give good quality metal.

Neither of these two methods met all of the desired requirements as processes for large-scale low-cost production of high purity uranium metal. Production was stepped up, however, by both of these methods beginning early in 1942 and plans for even larger expansion of the electrolytic plant were shaping up when the practicability of the uranium tetrafluoride-calcium process was demonstrated.

Efforts on the UF_4-Ca process were expanded and a few tons of the metal were produced in the chemistry laboratories at Iowa State College during the latter half of 1942 while a separate building on the campus was being remodeled and furnished to serve as a small production plant. Meanwhile, efforts were also directed toward the experimental development of the process employing magnesium in place of calcium; and as a result early in 1943 all uranium metal production was converted from the calcium to the magnesium reduction of the tetrafluoride.

This first uranium metal production plant employing the UF_4Mg process served not only to supply metal for experiments and for charging atomic piles but also served as a pilot plant where industrial technicians could inspect the process in operation and gain information for planning similar production plants elsewhere. The process proved to be one that could be readily expanded and it gave high purity uranium at a low cost. Over a thousand tons of uranium metal billets were shipped from the production plant (see Fig. 1) on the campus before industry took over uranium metal production entirely.

THE REACTION

There are certain advantages in using magnesium instead of calcium for the reduction of UF_4. The purity of the uranium metal product depends largely on the purity of the materials that go into the charge and the materials that the metal contacts before solidification. Commercial-grade magnesium generally has less contamination than commercial distilled calcium with regard to undesirable elements that might contaminate the uranium. Furthermore, the weight of calcium required to reduce a pound of

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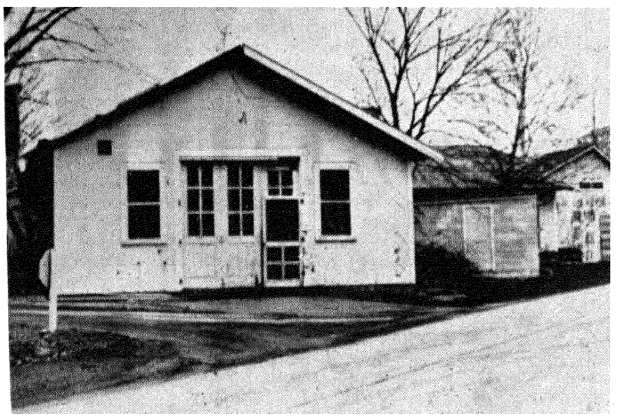

Figure 1. First large-scale uranium metal production plant in America

uranium is about 1.6 times as great as the weight of magnesium required for the same reduction. In addition, the cost per pound of the calcium may be five to ten times the cost per pound of magnesium. These factors as well as relative availability favored magnesium and made it desirable to explore the possibility of working out conditions for using magnesium instead of calcium in the reduction of UF_4.

Some of the requirements of the operating conditions necessary to achieve the desired results in the magnesium reduction can be introduced by first considering the well-known process of reducing UF_4 with calcium. If a mixture of UF_4 and excess Ca metal at room temperature is ignited at some point by means of a hot wire or a fuse, the reaction is propagated rapidly throughout the entire charge. The heat of the reaction is sufficient to heat both products, uranium metal and calcium fluoride, to a temperature well above their melting points. The liquid products then separate readily because of the difference in their densities.

The heat generated by the reaction between UF_4 and magnesium metal is about 45 kcal less per gram-atom of uranium formed than by the corresponding reaction employing calcium metal. The melting point of MgF_2 differs only slightly from that of CaF_2. Experimentally, it has been found that the heat generated during the reduction with magnesium is not adequate, by itself, to give the necessary fusion of the products. If heat is added, however, to the charge before or during the reaction, the necessary temperature for fusion and separation may be attained in the magnesium process.

This heat can be added by mixing in the charge an agent which affords an auxiliary reaction that generates excess heat on its own to serve as a thermal booster to the main reaction. If such a charge containing adequate booster at room temperature is ignited by a hot filament, the reactions will proceed spontaneously and give massive metal well separated from the slag. A mixture containing 7 mols of UF_4 to 1 mol of $KClO_3$ and a small excess of magnesium will behave in this manner.

A more convenient method of accomplishing this same objective is to preheat the unadulterated charge of UF_4 and Mg to ignition. The heat added to the charge before ignition and that of the reduction reaction together can be sufficient to yield the products in the desired molten condition.

In the calcium reduction, the charge can be placed in an open vessel and very little calcium metal will be lost by vaporization during the reaction. However, in the magnesium reduction the boiling point of the magnesium metal is well below the melting point of the slag, making it essential that the reaction by this process be carried out in a closed vessel. The vapor pressure of excess magnesium metal at the peak temperature is well above one atmosphere and this pressure tends to drive the chemical reaction in the desired direction.

The reaction between uranium tetrafluoride (green salt) and magnesium metal,

$$UF_4 + 2Mg \rightleftharpoons U + 2MgF_2$$

when carried out under proper conditions in a closed vessel will then generate sufficient heat to reach a temperature at which the products of the reaction are molten. The dense liquid uranium metal collects to form a regulus, with the molten magnesium fluoride slag on top. After allowing the products to cool to near room temperature, the reaction vessel can be opened and the massive metal recovered.

THE REACTION BOMBS

The reaction vessels employed in the very early experiments were made from iron pipe of diameters up to four inches and in lengths of six to twelve inches. However, for the various stages of the work described here, the vessels were made from sections of standard-wall seamless pipes that ranged in sizes from six to thirteen inches inside diameter. The lengths of these pipe sections ranged from about 36 inches to 45 inches, with the greater lengths generally employed with the larger diameters. A companion flange was attached at one end of the pipe section and a welded-in steel plate closed the other end to form a crucible. A blind flange was bolted to the companion flange for closing this crucible, which was then referred to as a bomb.

As experience was gained on small scale reductions and as more materials became available, the larger sizes of bombs were cautiously tried for the reductions. Only a few experimental reductions were made in four-inch-diameter bombs. A rather large tonnage of metal was produced by reductions in six-inch-diameter bombs, 36 inches in length. The size of charge was stepped up for a few eight-inch bomb reductions before increasing the bomb size to ten inches in diameter by 42 inches in length for further tonnage production. The regulus of massive uranium metal produced in a bomb reduction was referred to as a "biscuit." Biscuits were obtained in good yields from charges containing 56 pounds of UF_4 in the six-inch bombs, 180 pounds of UF_4 in the ten-inch bombs and 318 pounds of UF_4 in the thirteen-inch inside-diameter bombs. An average of 98.3% yield of biscuit metal was produced in the

thirteen-inch bombs after determining their proper operating conditions. The six-inch and ten-inch bombs also yielded about 98% of biscuit metal under favorable conditions. Since our plant grew up from a laboratory scale it was not highly mechanized for handling the larger biscuits and only rather limited special production was carried out in bombs larger than ten-inch diameter.

LINING THE BOMB

A rather high temperature is reached by the products of the reduction reaction and it is necessary that interaction between the charge and the steel bomb be prevented. A finely ground refractory material is used as a bomb liner to keep the molten mass and the magnesium vapor from attacking the bomb walls. Such attack would cause contamination of the uranium and possible failure of the bomb. The quality of this liner material and care in the lining operation are very important to the success of the reduction.

The lining operation starts with placing the empty bomb crucible on an air-operated jolting table. Sufficient powdered refractory is placed in the crucible to form a layer about one inch thick on the bottom. This is jolted for a few minutes and the operation stopped. A mandril, preferably made from metal tubing and closed on the ends, is inserted in the crucible and rests on this bottom liner. The mandrils for the larger crucibles are an inch or so less in diameter at the bottom than the inside diameter of the crucibles. These mandrils are tapered slightly, being a fraction of an inch larger in diameter at the top. The mandril is centered in the crucible and then more refractory liner material is introduced into the annular space between the mandril and the crucible wall. This loose refractory is jolted down and more is added (see Fig. 2) until the entire annular space is filled. The top region of the refractory liner is further rammed by means of a weighted metal cylinder that fits in the annular space at top.

During the jolting operation it is essential to maintain the mandril in the center of the crucible for uniform wall thickness and also not to allow it to sink and thus produce a thin liner on the bottom. The mandril is constructed with a small plug that fits flush on the bottom face of the mandril. This plug is attached to a rod which protrudes at the top of the mandril. Removal of this plug allows air to enter at the bottom as the mandril is slowly and carefully removed from the lined crucible (see Fig. 3). A properly lined crucible will have a lining that is strong and difficult to impress with the fingers (see Fig. 4).

CHARGING AND CLOSING THE BOMB

Proper amounts of finely ground UF_4 and granular magnesium are thoroughly mixed in preparing the charge. This mixed charge is emptied from the mixer into the refractory-lined crucible through a funnel. The charge is rammed down with care (see Fig. 5) so as not to disturb the liner. The amount of the charge is controlled so that it fills the crucible to about three inches from the top.

A thick graphite disc (or cake) slightly larger in diameter than the lined cavity above the charge is then forced down on top of the charge (see Fig. 6). The top section of the liner above the charge is then

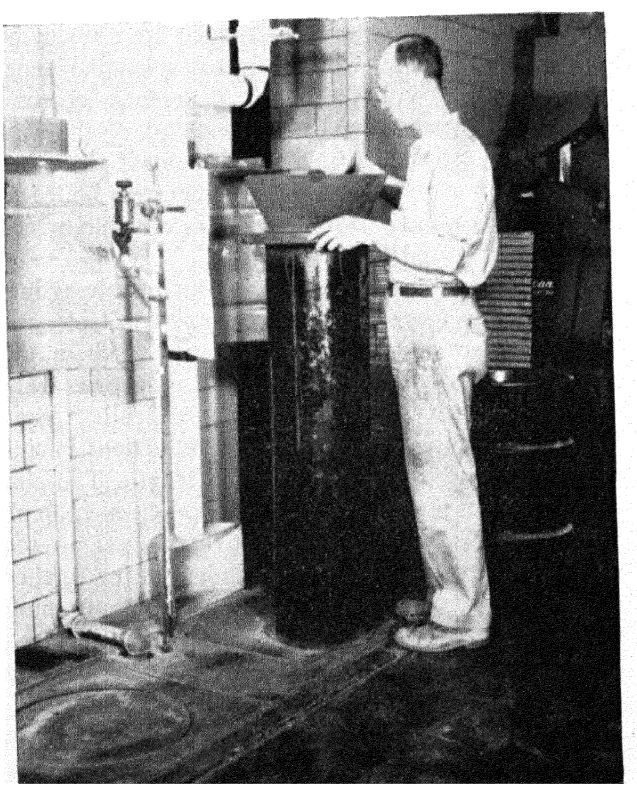

Figure 2. Adding refractory during jolt-packing of the liner

Figure 3. Removing mandril from lined crucible

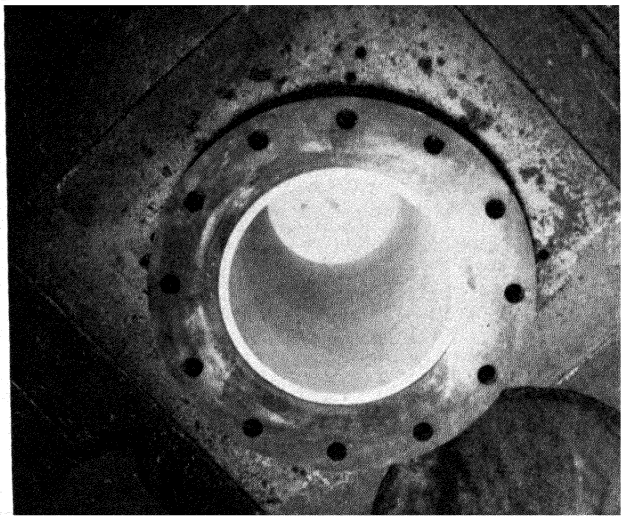

Figure 4. The refractory liner

re... and packed by hand to cover the graphite disc, or cake, with the liner material. A straight edge is then used to level off the liner top even with the machined surface of the companion flange (see Fig. 7). The machined face of a blind flange is then bolted in place on the machined surface of the companion flange. No gasket material is used. The charged bomb is then placed in a furnace, or heat soaking pit (see Fig. 8), to initiate the reaction, or to fire.

THE BOMB FURNACE AND FIRING TIME

One design of furnace that serves quite well for the uranium reduction process is shown by the drawing in Fig. 9. It is gas fired and has its top at floor level. The particular drawing shows a two-bomb capacity section of such a furnace that may extend for a number of such sections. Only one bomb is shown in position.

The furnace temperature for best operation will depend on a number of factors such as size of bomb, rate of furnace recovery on introduction of a cold bomb, point at which temperature is measured and other factors associated with the bomb lining and charge. The optimum temperature of operation will generally be within the range of 550°C to 700°C with the thermocouples positioned as in Fig. 9. The time required for the reaction to initiate will usually be longer, the larger the bomb and the lower the furnace temperature. As much as three and a half hours are required for ignition to take place in the thirteen-inch diameter bombs with the furnace temperature at 565°C while the ten-inch bombs require about two and a half hours and the six-inch size about one and a half hours with the furnace operating at the same temperature.

When the reaction takes place, sufficient agitation of the bomb occurs for a contact microphone on the opposite end of the reaction indicator rod (see Fig. 9) to indicate the event. After a minute the reaction is essentially settled and the entire metal phase

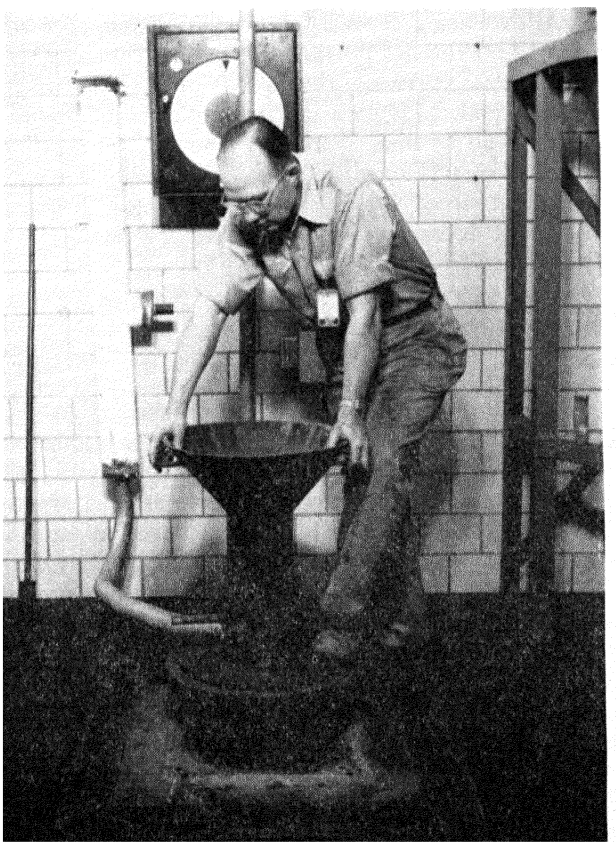

Figure 5. Ramming charge with funnel

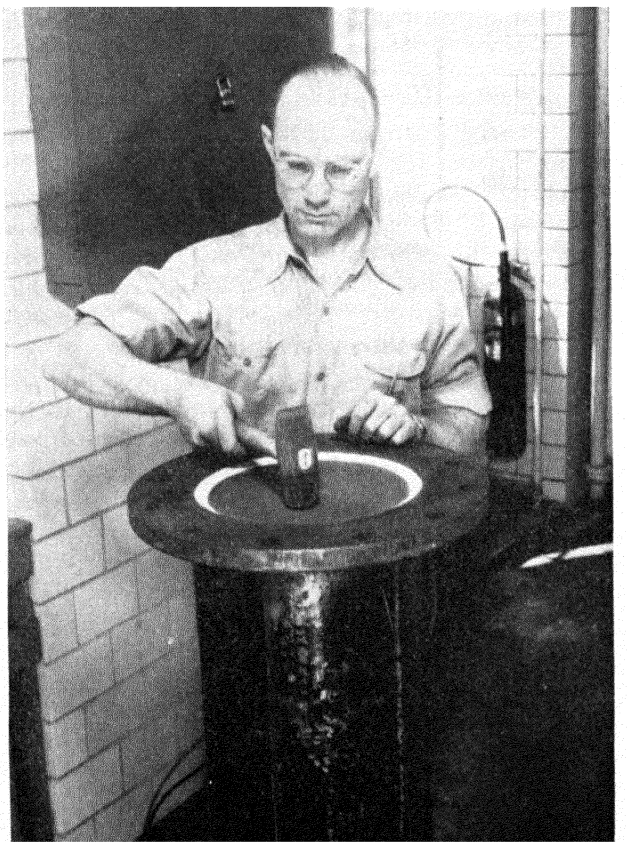

Figure 6. Covering charge with thick graphite cake

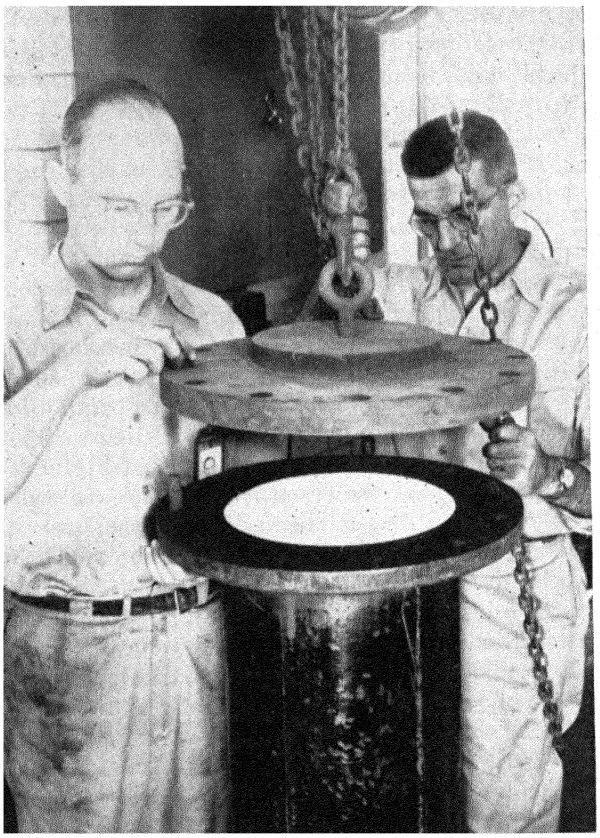

Figure 7. Liner on top of graphite cake leveled off and ready for cover flange

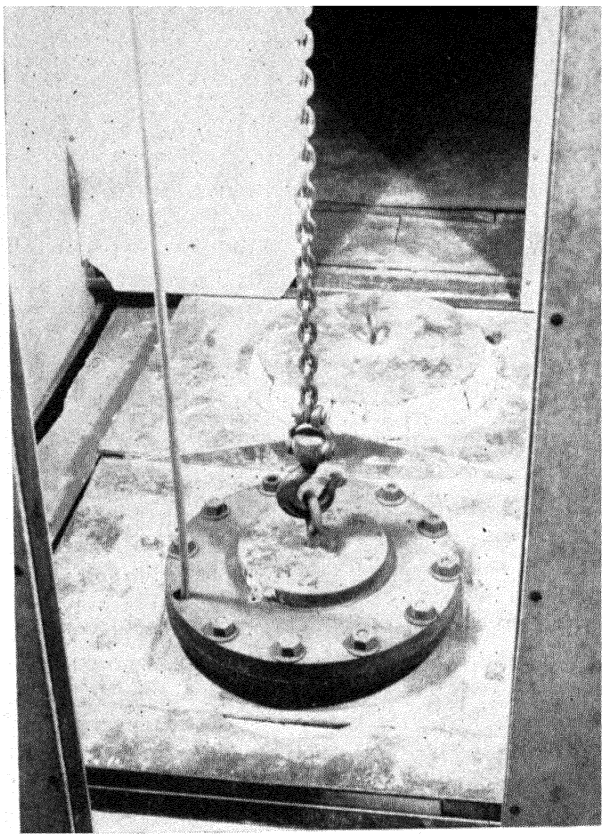

Figure 8. Charged bomb in furnace. Reaction indicator rod at left on bomb lid

may remain molten for at least ten minutes in the larger sizes of bombs.

UNLOADING THE BOMB

After the reaction has subsided the bomb is removed from the furnace and allowed to cool in an upright position in air until its temperature is near that of boiling water. It is then sprayed on the sides with cold water until its contents are near room temperature. The cover plate is then removed and the bomb inverted on a jolting table to remove the metal biscuit, the slag and the liner.

Adhering slag is then broken or chipped loose and the cleaned metal is weighed and delivered to the casting room. The bomb crucible is cleaned and returned to the loading line for another charge.

QUALITY OF MATERIALS

In the calcium reduction of uranium tetrafluoride there is sufficient heat and driving power for the reaction that preheating of the charged bomb is not necessary, and good yields of biscuit metal can be obtained with relatively low-grade liner material and low-grade uranium tetrafluoride. However, in the magnesium reduction, especially by the preheat process, the yield of metal and degree of slag separation are sensitive to the qualities of materials employed.

The specifications for the uranium tetrafluoride (green salt), the liner material and the magnesium metal are dependent upon the yield and quality of metal that are acceptable. For example, suppose that the green salt that is readily available analyzes 96% UF_4. It is an experimental fact that, other things being equal, a higher percentage of UF_4 gives a better yield of final metal. Whether or not this possible increase in metal yield would warrant the extra treatment necessary in making the better grade of UF_4 will depend on economic factors that exist at the particular location.

Some of the factors to be considered in choosing materials for this process are given here.

The Green Salt

Uranium tetrafluoride can be produced from UO_2 and other compounds of uranium by a number of processes. Regardless of the process employed in its manufacture, there are a few common qualities of the green salt that should be considered as bearing upon its behavior and metal yield and quality.

It is quite obvious that certain elements if present in the green salt would be carried into the biscuit metal and be present as impurities in the final metal. Uranium ore processing and purification by liquid-liquid extraction, as described elsewhere in the Proceedings of this Conference, are sufficiently developed to give high purity UO_2 and other intermediates. Impurities of the type considered here that are carried by UF_4 would most likely come from reagents and equipment employed in the conversion of these intermediates.

High moisture is detrimental in the charge regardless of its source. It may cause side reactions and lower the yield and quality of the product. Furthermore, if a large amount of H_2O is present when the reaction fires, the resulting gas pressure may be sufficient to cause failure of the bomb.

The oxygen content of dry green salt may be in the form of UO_2F_2 or perhaps as UO_2. The higher the oxygen content, the lower the UF_4 content and, other things being equal, the lower the biscuit metal yield and poorer the slag separation. Green salt analyzing 96% UF_4 can be employed to give fair yields of metal but 98% or higher UF_4 content is preferred.

The packing density of the green salt is a factor that is dependent on the method of preparation and particle size. A dry-process UF_4 may have a packing density of greater than 3.5 gm/cm³ while a wet-process UF_4 may have a packing density of only about half this value. The higher the packing density, the greater the amount of charge that can be placed in a certain volume and the greater the amount of heat developed per unit area of container wall. The charge with higher packing density generally has better heat conductivity which would result in greater heat penetration into the charge before the surface reached ignition temperature. For good yields a packing density of 3.0 gm/cm³ or greater is desired for the green salt.

Related to the packing density and a factor to be considered in bomb reductions of UF_4 with magnesium is the fineness of grind, or particle size distribution. The particle size distribution, however, can vary over rather wide limits without major effects on the behavior of the green salt. Green salt that met other qualifications and which came within the following ranges of sieve analyses, reduced with good yields:

Standard sieve no.	*% passed*
60	96 to 99
80	91 to 95
100	85 to 92
200	62 to 75
325	52 to 62

The Liner Material

Since small fractions of the impurities in a refractory liner are picked up by the metal during the vigorous reduction reaction, it is essential that the refractory be produced from good quality starting materials. Liner materials that were successfully employed in the early production plant included dead-burnt high-calcium lime and electrically-fused dolomitic oxide, both in a fine state of division. The sources of limestone and dolomite were selected on the basis of purity, and the final refractories contained about 500 ppm iron, 60 ppm manganese and 5 to 10 ppm boron.

The evolution of water or other gases from the liner before or during the main reaction can be detrimental. It is essential then that the finely ground liner material have a low loss of weight on ignition and that it be protected from picking up moisture or gases before placing in use. Rapid evolution of gas in the liner during the reaction may cause large amounts of the liner to become mixed with the reacting charge or cause complete liner failure resulting in a blow-out. Loss of weight on ignition by the two refractory materials mentioned ranged from 0.20% to 0.90% for the dead-burnt lime, while for the electrically fused dolomitic oxide the value of 0.24% was a maximum. Although the dead-burnt lime cost much less per pound, the large variation in its loss on ignition made it the less desirable refractory of the two.

Evolution of water vapor from the liner during the preheat period can cause side reactions that lower the yield of metal. As a charged bomb heats in the furnace the liner gets hot first. If moisture is released by the liner it can pass into the charge and react with the UF_4 to form UO_2 and HF. The HF can then return to the liner and form a fluoride and more water to again hydrolyze more UF_4. The net result is a layer of UO_2 formed next to the liner. When the bomb fires, the magnesium does not effectively reduce this UO_2; therefore, the yield of metal is lowered by the slow evolution of H_2O from the liner. A measure which tends to correct this effect is to add a few per cent of very fine magnesium or calcium metal to the refractory powder before packing the liner. Then, as the water is released in the hot liner, there is hot magnesium or calcium present to react with the water to form hydrogen. This hydrogen may diffuse out into the charge and eventually escape between the flanges at the top of the bomb.

Another property which is related somewhat to the quality of liner that a certain refractory will make is the packing density. The greater the sintering or degree of fusion of the oxide, the greater its packing density and the more inert is the material to picking up moisture or carbon dioxide. The dead-burnt lime has a packing density of about 1.75 gm/cm³ while the electrically-fused dolomitic oxide has a packing density of about 2.0 gm/cm³. Ordi-

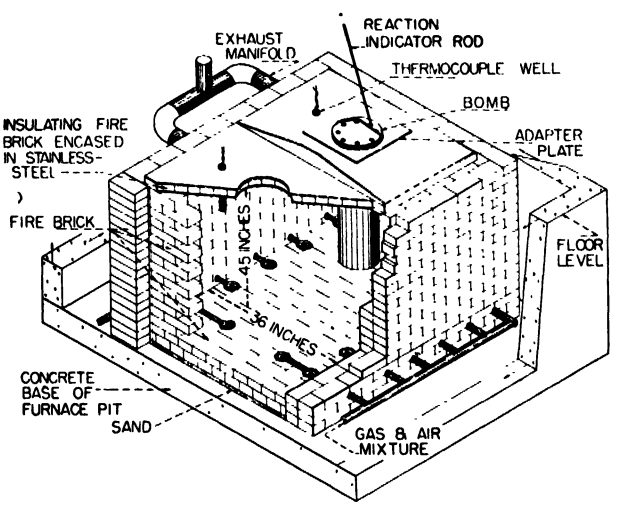

Figure 9. Gas-fired bomb furnace

nary high-calcium lime and dolomitic lime show packing densities of about 1.45 and about 1.35 gm/cm^3 respectively, and they are unsatisfactory as liner materials.

Although many batches of the dead-burnt lime did perform very satisfactorily, it was entirely replaced by the electrically-fused dolomitic oxide which performs consistently well. The distribution of particle size of the liner material can vary over wide limits and still give a hard and strong jolt-packed liner that will stand up well during the reaction. A sieve analysis that represents a number of batches of electrically fused dolomitic oxide is given here.

US standard sieve no.	*% passed*
45	98
80	78
170	53
325	40

The Magnesium

In the early work, magnesium available from different manufacturers was tested in an attempt to determine the source of the best magnesium for use in the reduction of UF_4. A redistilled electrolytic magnesium, a redistilled carbothermic magnesium and a number of other batches of magnesium made at different plants employing the ferrosilicon process were tested.

Considerable variation seemed to exist in the reduction behavior of all batches of magnesium metal. The variations observed in the behavior of batches from the same producer were as great as were observed between batches of magnesium made by different processes. At the time of these tests, the quality of the liner material and the quality of the green salt were varying widely. Much of the scatter of individual values in the data obtained in the magnesium tests was, no doubt, attributable to the other materials.

On the average, better results were obtained, however, with magnesium from a plant employing the ferrosilicon process, so production was standardized on magnesium from this one source. The magnesium from the selected source consistently met all purity requirements as far as the regular chemical analysis was concerned. This was true also of the magnesium made by the other producers. Some differences were observed in the macroforms of the crystals and in the physical shapes of the finely ground particles of magnesium from the various sources. Neither of these characteristics, however, could be related to the performance of the magnesium in the reduction. The possibility existed that the erratic behavior of different batches of magnesium even from the same producer was due to variations in operations connected with the processing at the magnesium metal plant. The temperature of the metal when exposed to air on removal from the magnesium production retort as well as possible air leaks in the vacuum system might have developed conditions that resulted in the variations experienced here with different batches of Mg.

Most of the magnesium from the selected source was supplied in the form of hollow cylinders, or muffs, that consisted essentially of matted and finger-like crystals. The muffs were about ten inches in diameter. They were formed on the condenser as the crystals grew from the magnesium vapors produced in the ferrosilicon reduction of magnesium oxide. The crystal orientation in the muffs was somewhat radial with little indication of any tendency of the crystals to grow together. The muffs were readily broken into smaller pieces by blows with a sledge hammer. These pieces were then cut to hand-size chunks on a punch press fitted with a cutter blade. These magnesium chunks were passed over a magnetic separator to remove any tramp iron before feeding the chunks to the next machine.

These chunks were reduced to pieces about one-fourth of an inch in size by a cutter-type mill. The cutting in the mill was done by heavy knives mounted in the face of a heavy rotor; the knives passed within a fraction of an inch of heavy metal bars. With the rotor operating at high speed, the chunks of magnesium were readily cut to pass through a screen in the bottom of the mill. This mill was a standard machine of the type that is employed in shredding wood and paper and is often referred to as a "garbage hog." The quarter-inch size product from this mill was passed over a magnetic separator to protect the more delicate machine used in cutting the magnesium to a finer size.

The next machine was of a type that consisted of a number of long knives mounted on the outer edge of an open frame-work reel that rotated on an axis. In the operation the rotating knives passed within a few thousandths of an inch of a number of stationary knives mounted in the housing of the mill. This machine, except for its screens, was a standard mill used for cutting corn and other grain to fine particles. This cutting action reduced the magnesium to sizes that would pass through a bottom screen.

The magnesium was then passed over a screen to remove the fines and the dust. Samples were taken for chemical and sieve analyses. The approved ground magnesium was passed over a magnetic separator just prior to weighing for the charge. The particle size distribution of most magnesium cut in the manner described here is represented as follows:

US standard sieve no.	*% passed*
10	90–99
20	25–55
30	10–35
40	3–15
60	0–1

Since magnesium does react slowly with air, it is considered advisable to grind the magnesium at such time that the finely divided metal will not have to remain in storage for long periods.

SOME OPERATIONAL CONSIDERATIONS

Excess Magnesium

It has been established experimentally that an excess of magnesium over the stoichiometric amount

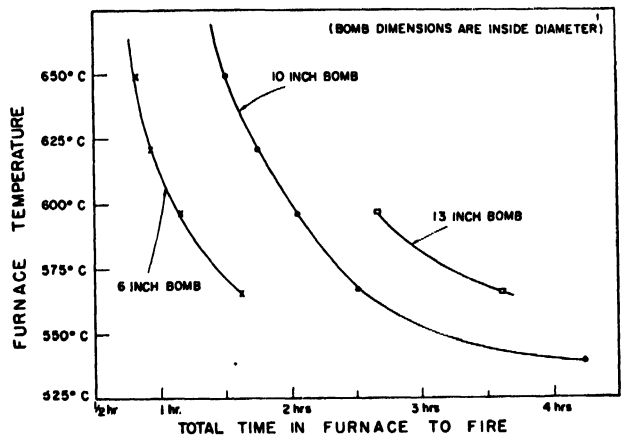

Figure 10. Variation of firing time with furnace temperature

for reaction with the UF_4 in the charge is essential to obtain better yields of uranium metal. As the per cent of excess magnesium increases from zero there is a sharp increase in biscuit yield. This increased yield reaches a maximum and rather abruptly levels off on a plateau for higher percentages of excess magnesium. The amount of excess necessary to reach this maximum with good quality materials varies slightly with production sizes of bombs; the larger bombs require slightly less excess than the smaller bombs. Ten-inch and larger bombs require about 5% excess and a six-inch bomb requires approximately 7% excess. Small experimental bombs employing only a few pounds of UF_4 may require 20% to 30% excess magnesium to reach the maximum.

Liner Thickness

The material, the compactness and the thickness of the refractory liner in a bomb are factors that

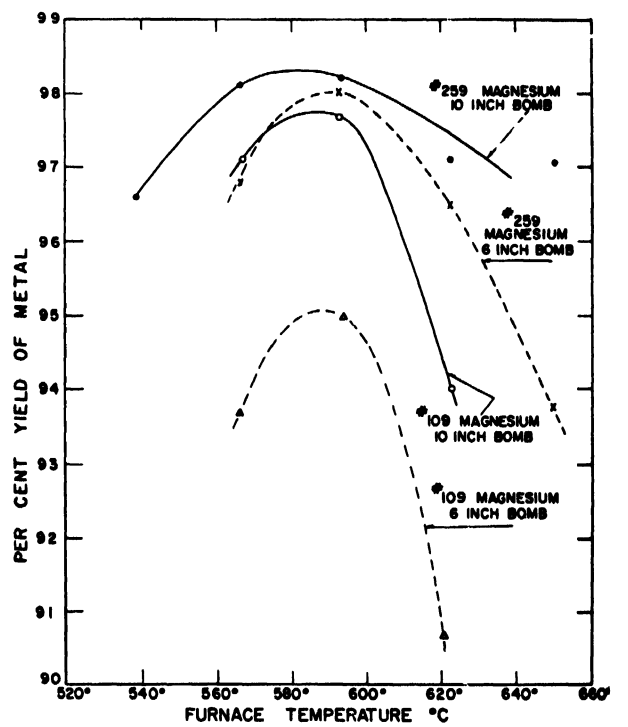

Figure 11. Variation of yield of metal with furnace temperature

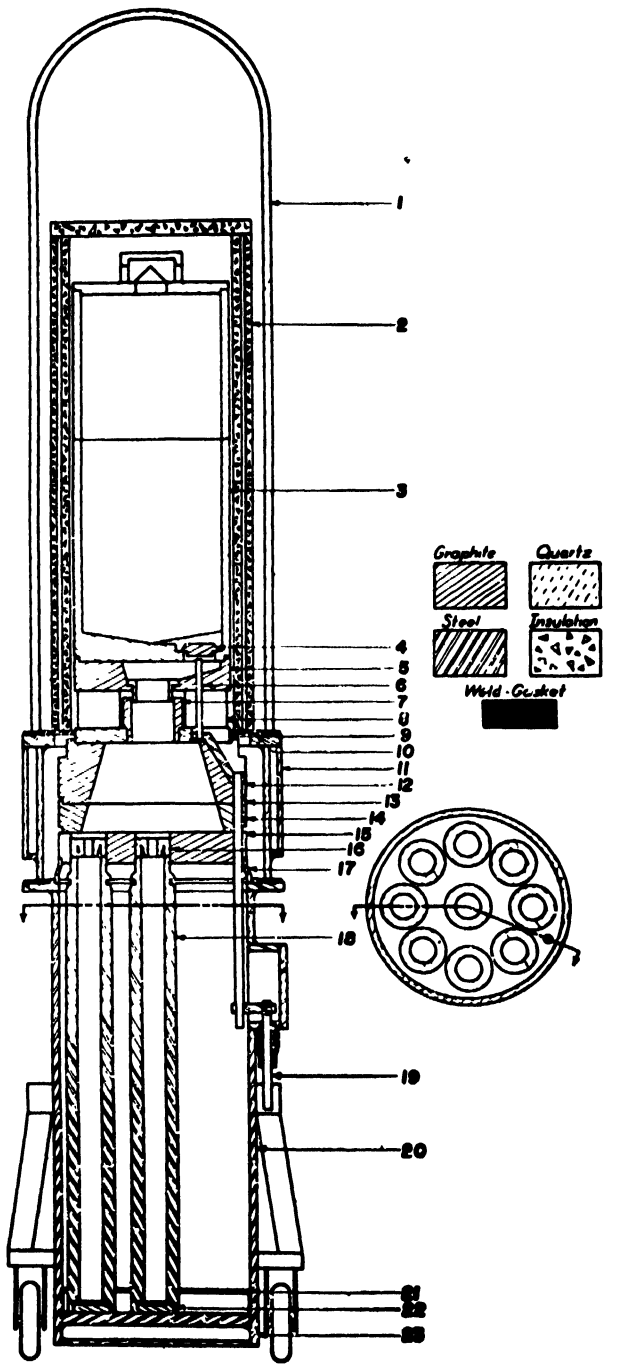

Figure 13. Casting furnace for rods: (1) 15 in. od quartz tube; (2) sillimanite insulation shields; (3) graphite crucible; (4) graphite valve disk; (5) graphite spillway; (6) graphite push rod; (7) graphite chimney; (8) insulation base; (9) graphite cover plate; (10) steel ring insulation support; (11) steel water jacket; (12) graphite reservoir (upper section); (13) graphite reservoir (lower section; (14) offset steel push rod (upper section); (15) graphite feedway plate; (16) graphite plug with orifice; (17) steel ring feedway support; (18) steel mold; (19) offset steel push rod (lower section); (20) steel vacuum jacket; (21) steel template; (22) graphite plug; (23) water-cooled base. (Thermocouples, vacuum connection and charge are not shown in this figure)

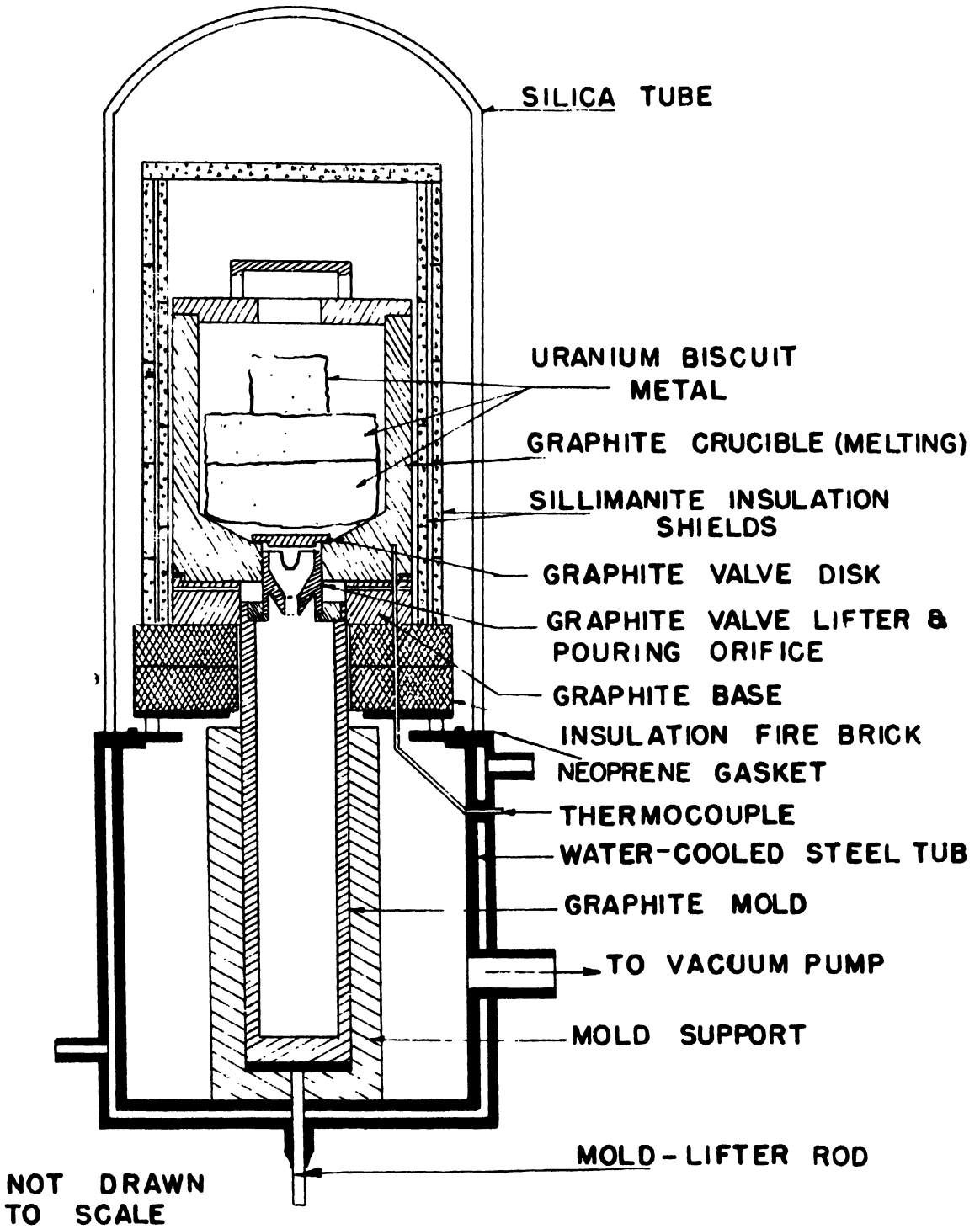

Figure 12. Uranium casting unit

contribute to the success of the reduction operation. The flow of heat to the charge before ignition must take place through this medium which also must serve as an inert heat insulator after the reaction. A liner that is too thin might conduct heat too rapidly and tend to cause firing before sufficient heat enters the major part of the charge. Then too, if a charge fires properly with a thin liner the high heat may reach the steel bomb wall and lower its strength while pressure exists in the bomb, resulting in a blow-out. Refractories such as magnesium and calcium fluorides require greater thicknesses because of their low melting points. The refractory oxides employed in the development work have high melting points and can be employed in thicknesses of less than an inch in the production-size bombs mentioned here. Actually ½-inch, ⅝-inch and ¾ inch walls were employed in the biscuit region of the 6-inch, 10-inch and 13-inch bombs, respectively. Since the mandrils were tapered slightly the walls were thinner at the tops. Exact centering of the bottom end of the mandril was done by means of a ball gage of the proper size. The thickness of the liner on the bottom of the bombs was usually about one inch.

Preparing the Charge

In the hand operations employed in the plant at Ames, the separate ingredients of the charges were merely poured into weighing buckets on "over-under" weighing scales that carried tare weights for the buckets. The weighed magnesium and green salt were dumped into a batch blender of the double-cone type. A thorough mixing of the charge is essential for best results. Furthermore, the mixed charge should be well packed into the lined crucible in order to increase the charge density and to get better heat conductivity.

Protection Walls Around Furnace

Due to the fact that the internal pressure of the bomb at its peak inside temperature is well above atmospheric pressure it is essential that the operators be protected from possible bomb failure. Brick walls around the furnace working space have been found adequate for the protection of operators. Ports through these walls permit the necessary operations. Furthermore, operators should not remove any fired bomb from a furnace until the reaction has fully subsided. Hot spots may develop on the bomb at areas where the liner is thin and at areas having partial liner failure. Complete failure of the liner at a point usually results in a blow-out. Although blow-outs were not uncommon in the early development days, as better oxide liner materials became available and lining techniques improved, blow-outs were rare indeed.

Furnace Temperature and Firing Time

The design of the furnace can vary widely. Whether the bombs are heated by gas burners, electrical resistance heaters, radiation heaters or by induction makes little difference so long as the heat gets to the charge with the proper rate and distribution. Generally the higher the temperature of a furnace and the smaller the bomb diameter the shorter the time of heating to produce ignition. Some data

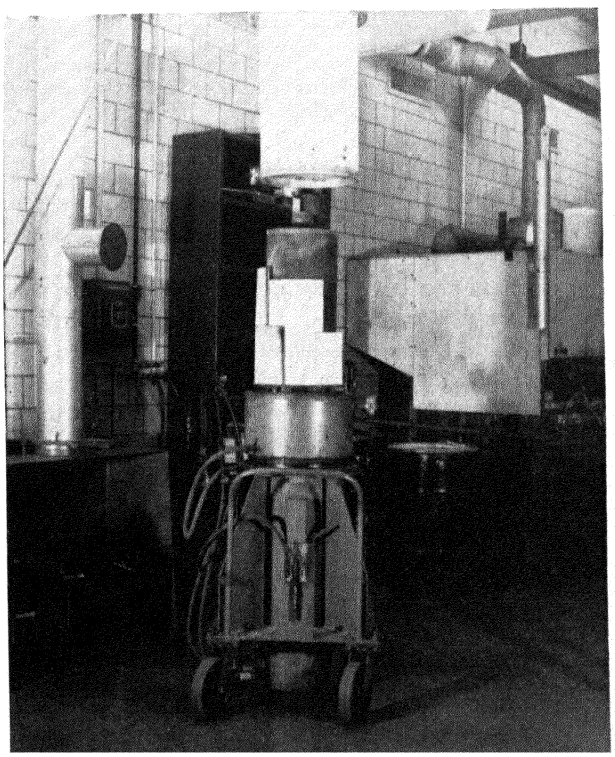

Figure 14. Rod casting furnace with some insulation shields in place. Silica tube hangs overhead

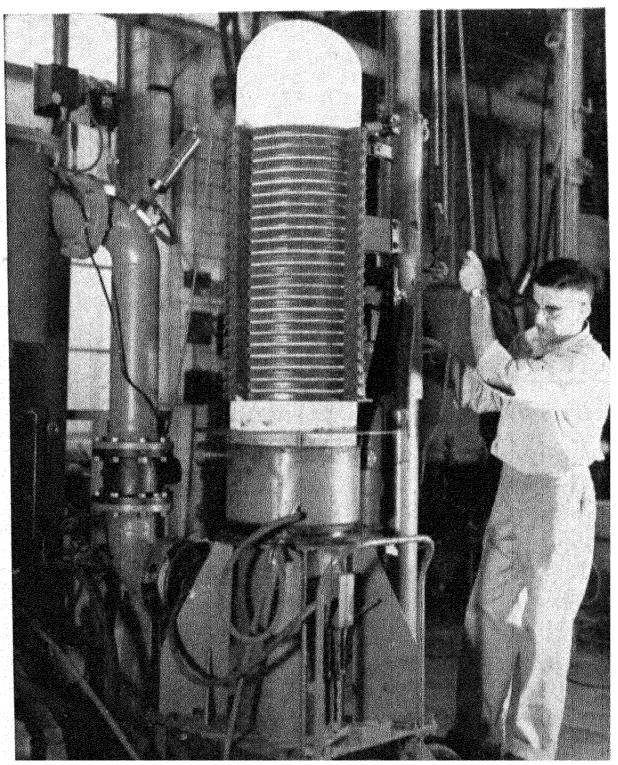

Figure 15. Adjusting position of induction coil preparatory to heating the charge in rod casting

on firing time as related to bomb size and temperature of a furnace, such as that described earlier, are shown in Fig. 10. The higher temperatures that shorten the soaking time may or may not be advantageous from the standpoints of yield of metal and furnace life.

Furnace Temperature and Yield

In tests to determine the relationship of yield to any of the numerous variables that bear upon the behavior of the magnesium reduction process, the furnace temperature must be given prime consideration. As an example of the importance of furnace temperature, results from a series of tests on two different magnesiums in two different sizes of bombs at various temperatures are shown graphically in Fig. 11. The green salt and liner materials were essentially the same in all of the reduction tests made in this series. It is to be noted that for all four curves, each of which represents one magnesium in one size of bomb, the biscuit yields exhibit essentially the same maximum with temperature. Furthermore, in these tests the ten-inch bombs yielded higher than the six-inch bombs with the same magnesium and at the same furnace temperature. In addition, the yields with one of the magnesiums were slightly more sensitive to temperature variations in both sizes of bombs. The essential difference in these two magnesiums was that No. 109 magnesium had been ground then stored for five months before the tests, while No. 259 was ground only five days before tests.

The curves shown in Fig. 11 are not to be interpreted as representing the type of behavior to be expected in all such tests on materials. Some tests made on batches of liner material, green salt and magnesium, especially when the quality of each of these materials varied widely, have exhibited very flat curves, curves with two maxima, and curves with maxima shifted to higher or lower temperatures. Changes in furnace design and in position of the thermocouple would also cause shifts in such curves. Figure 11 does show that to be reasonably sure of getting the best yields with the materials and equipment available, tests of the kind described are essential. These tests may also include a standard casting operation and be based not on biscuit yields but on over-all yields of final cast metal.

CASTING URANIUM METAL

Early in 1942 the small castings of uranium metal that were being made in America were made by vacuum self-induction heating of uranium powder compacts supported in beryllia crucibles. On heating to high temperatures the liquid uranium metal would break through its tough oxide skin and flow through a grill and into a beryllia mold. Experimental work at Ames soon demonstrated that graphite crucibles could be employed for vacuum induction melting of uranium. The melting point of uranium was found to be about 1130°C and at pouring temperatures of up to 1300°C and even higher, the solubility of carbon in the uranium was not greater than a few hundred parts per million. In the early production plant, uranium was melted in a graphite crucible having a grill for the bottom to catch oxide skins as the metal flowed into a heated graphite mold below.

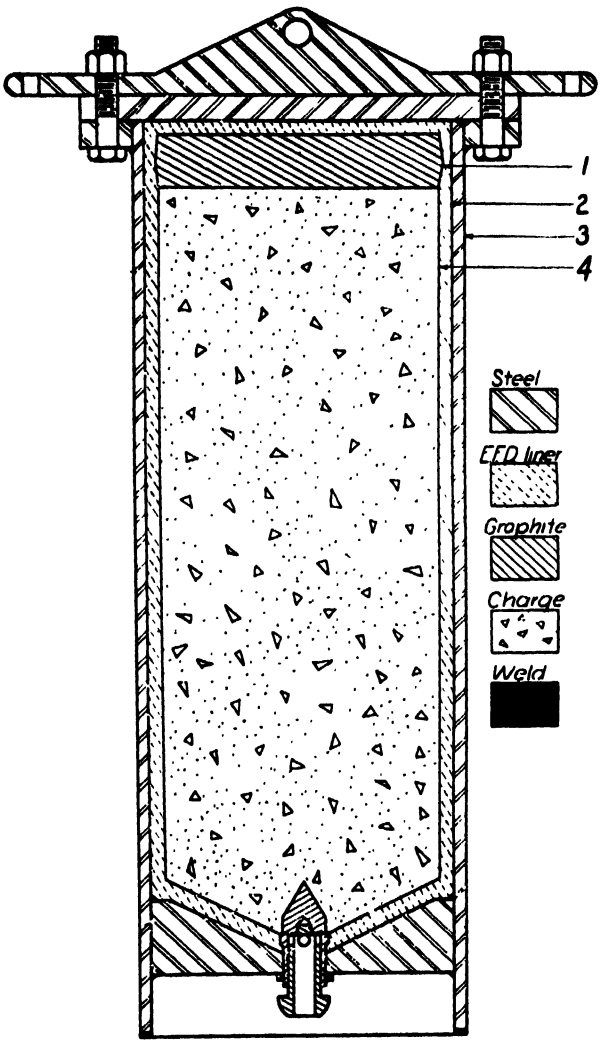

Figure 16. Charged direct-pour bomb ready for furnace: (1) graphite cake; (2) refractory liner; (3) bomb wall; (4) charge of UF_4 and Mg

In certain phases of uranium metallurgy there may develop concentrations of materials that present chemical and radiological health problems. The vacuum melting and casting operation does give some concentration of such materials especially in the flue dust and in the dross from graphite melting crucibles.

Casting an Ingot

The uncertainty of pouring temperature and rate of flow in the grill-type casting set-up made it necessary to work out designs for melting and casting units that would give better control of the operation for larger sizes of ingots. The designs for these larger casting units were modified from time to time as sizes and shapes of castings were changed.

One design that can be used for vacuum casting a single uranium ingot is shown in Fig. 12. The heating is effected by a hoist-type induction coil (not

shown) which is lowered to its operating position around the silica tube. Heat is generated in the graphite crucible and its temperature is followed by means of the thermocouple. When the metal is at casting temperature it is poured into the mold by opening the valve in the crucible by means of an upward thrust on the mold-lifter rod. The valve lifter is mounted in the top of the mold. This thrust lifts the mold and the valve lifter which in turn lifts the valve disk. The valve disk is forced far enough from its seat to float to the top of the melt as the uranium liquid flows through the orifice and into the mold. Ventilation of the mold cavity takes place through ports (not shown) in the valve lifter below the orifice.

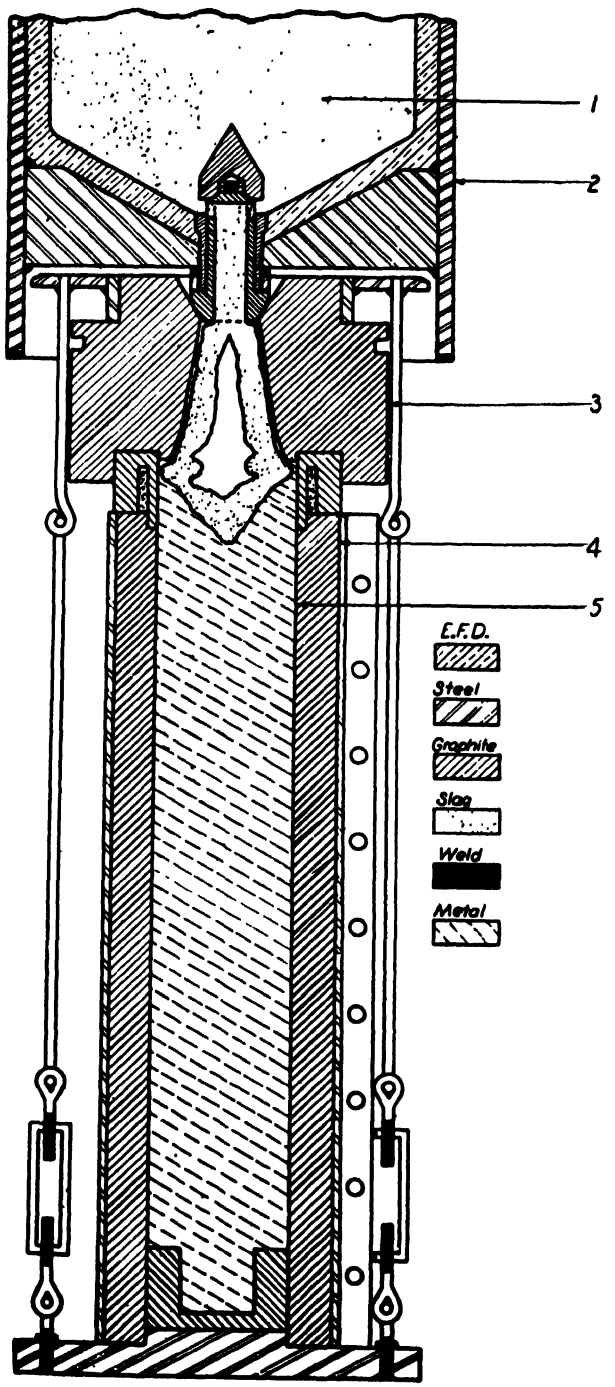

Figure 17. Solidified ingot and slag: (1) MgF_2 slag; (2) lower end of bomb; (3) mold cover; (4) mold; (5) uranium ingot. (Shrinkage of ingot not shown)

The ingot obtained by this process is cropped to remove the pipe and the resulting billet is an intermediate form for further fabrication into shapes.

The Casting of Rods

Furnaces for casting a number of rods at one pouring were set up early in the development work. A sketch of one of these furnaces is shown in Fig. 13. This furnace has a capacity to cast simultaneously nine uranium rods about 1½ inches in diameter by 29 inches in length. The charge of metal required is around 300 pounds.

Figure 14 is a photograph showing one stage in the assembly of the furnace when only a few of the sillimanite insulation sections are in place around the graphite melting crucible; the silica (or quartz) tube is hanging from above. The operator is shown in Fig. 15 adjusting the hoist type induction coil on the silica tube preparatory to the heating.

The melting pot or crucible of Fig. 13 has the valve disk to one side rather than in the center of the bottom of the melting pot. When the melt is ready for pouring by the thermocouple (not shown here) the push rod (No. 19) is given an upward thrust. This movement is transferred to another steel push rod inside, which in turn causes the graphite push rod (No. 6) to lift the valve disk (No. 4) from its seat. The metal flows through the valve and the opening in the graphite spillway (No. 5). From here the metal pours into the graphite reservoir (No. 12 and No. 13). From the reservoir, metal flows simultaneously through nine separate orifices (No. 16) in the feedway plate (No. 15) to nine steel molds (No. 18). On cooling, the rods are easily removed from their molds.

THE DIRECT-POUR PROCESS

In the bomb process described above the objective was to produce uranium metal which was allowed to solidify in the bomb and then, by means of remelting and casting, produce the desired shape of ingot. The objective of the process described briefly in this section is to cast the liquid metal, which results from the reduction reaction, directly into the desired shape of ingot.

The bomb, lined with electrically fused dolomitic oxide (E.F.D.) and charged with the usual mixture of UF_4 and magnesium, is sketched in cross section in Fig. 16. This bomb has a special bottom which accommodates a valve for pouring the molten metal when desired. This valve is inserted by a special adapter on the mandril used in the lining operation.

The charged bomb is placed in the furnace and a few minutes after it has fired, the metal is poured into a graphite mold that is in an assembly held rigidly together by turnbuckles. The ball face of the valve spout fits into a cone in the top face of

a graphite cover to the mold. In bringing the top of the mold and the valve of the bomb together sufficient pressure is exerted to force the valve spout up in the valve housing, thus permitting the metal to flow through the spout to the mold. A sketch that represents conditions after the metal has poured and cooled is shown in Fig. 17.

Bomb charges containing 318 pounds of green salt gave about 238 pounds of metal for each casting. The ingots when cropped below the pipe gave billets weighing about 220 lbs. Ingots produced by this process are exceedingly low in carbon content but are higher in magnesium and hydrogen content than metal melted and cast in vacuum as described in an earlier section of this report.

ACKNOWLEDGEMENTS

This report is based on the researches that were connected with the development of the Ames process for producing metallic uranium. The author wishes to emphasize that this work was a joint effort of many scientists and technicians. The program was directed by F. H. Spedding, W. H. Keller, C. F. Gray and the author.

Fundamental Considerations in the Reduction Processes of Thorium and Uranium

By B. Kopelman,* USA

The reduction processes leading to the formation of either thorium or uranium metal are associated with many difficulties attributable mainly to the stability of their compounds. As a consequence, both metals are highly reactive towards most substances, particularly at elevated temperatures, and contamination by the atmosphere or by reaction with containers occurs readily unless adequate precautions are taken.

Since conventional metal containers are easily attacked by both uranium and thorium at the temperatures existing during reduction, liners of refractory materials such as lime or magnesia become necessary to minimize contamination from this source. Both elements also react directly with nitrogen as is indicated by the negative free energy of formation of thorium nitride and uranium nitride (listed in Table I), so that either an argon cover or a high vacuum becomes necessary during reduction, particularly when high purity metal powder is desired.

When in a finely divided state, both elements combine spontaneously with atmospheric oxygen, even at room temperature, to form very stable oxides. This stability is also apparent in compounds such as the halides and becomes quite evident from a comparison of their free energy of formation to that of other similar compounds. A tabulation of these values at room temperature (298°K) appears as Table I and has been presented in kilocalories per gram-atom of non-metal, so as to facilitate the comparison.

Another measure of the stability of thorium and uranium compounds is the inability of hydrogen to reduce them to metal at temperatures approaching 2000°C. This is true for both the oxides and the halides as can be seen from the calculated free energies of reaction listed in Table II, and thus eliminates from consideration one of the most convenient methods of producing metal, gaseous reduction. To place thorium and uranium, in their proper perspective with respect to ease of reduction, the equilibrium concentration of water vapor-hydrogen in several metal-metal oxide systems has been calculated and is shown graphically in Fig. 1. From these curves, it becomes immediately evident that hydrogen containing 1 part of water vapor in 4×10^5 (log [conc. H_2O/conc. H_2] = — 5.6), such as is present in gas dried by activated alumina, will not reduce these oxides, thus placing them together with titanium, zirconium, aluminum, beryllium and magnesium in the class of difficultly reducible compounds.

Although there are many problems associated with the preparation of thorium and uranium metal, some of these difficulties are mitigated by the fact that ductility or workability of both is not critically dependent upon the absence of small amounts of gaseous impurities as is the case with metals such as titanium. This can be readily seen by comparing the effects of increasing oxygen and nitrogen content upon the ductility of pure thorium and pure titanium metal. As shown in Fig. 2,[1] the presence of 0.4% by weight of nitrogen decreases the per cent reduction in area measured during the tensile testing of titanium by a factor of four, whereas that of thorium is decreased by a factor of only 1.2. Though not quite as sensitive as the nitrogen content, the presence of oxygen also has a marked effect on titanium as compared to thorium. Since reduction in area is the maximum amount that the cross-sectional area of metal can be reduced before fracture occurs, it is directly related to the ductility of the material, and therefore a good indication of its workability.

Thus it can be seen that the difficulties entailed in reducing thorium and uranium are compensated, at least to a large degree, by the ability of both metals to tolerate comparatively high impurity levels of nitrogen and oxygen and still maintain their desirable mechanical properties.

REDUCTION BY THE ACTIVE METALS

Among the common active metals, calcium and magnesium are most often considered as possible reducing agents for the oxides of thorium and uranium. Of these, magnesium is considerably poorer from a thermodynamic viewpoint, particularly in the case of thorium where, as can be seen in Table III, the reaction reverses itself at high temperatures. However, because of the higher cost of calcium metal, reduction processes based upon the use of magnesium are more desirable economically.

Although reduction of the halides is considerably less difficult, the use of oxide as the starting material has definite economic advantages, primarily the elimination of a halogenating step in the processing cycle of these metals. On the other hand, calcium is, thermodynamically, by far superior to magnesium, although any economic advantage obtained through use of the oxide route would be cancelled or, at the

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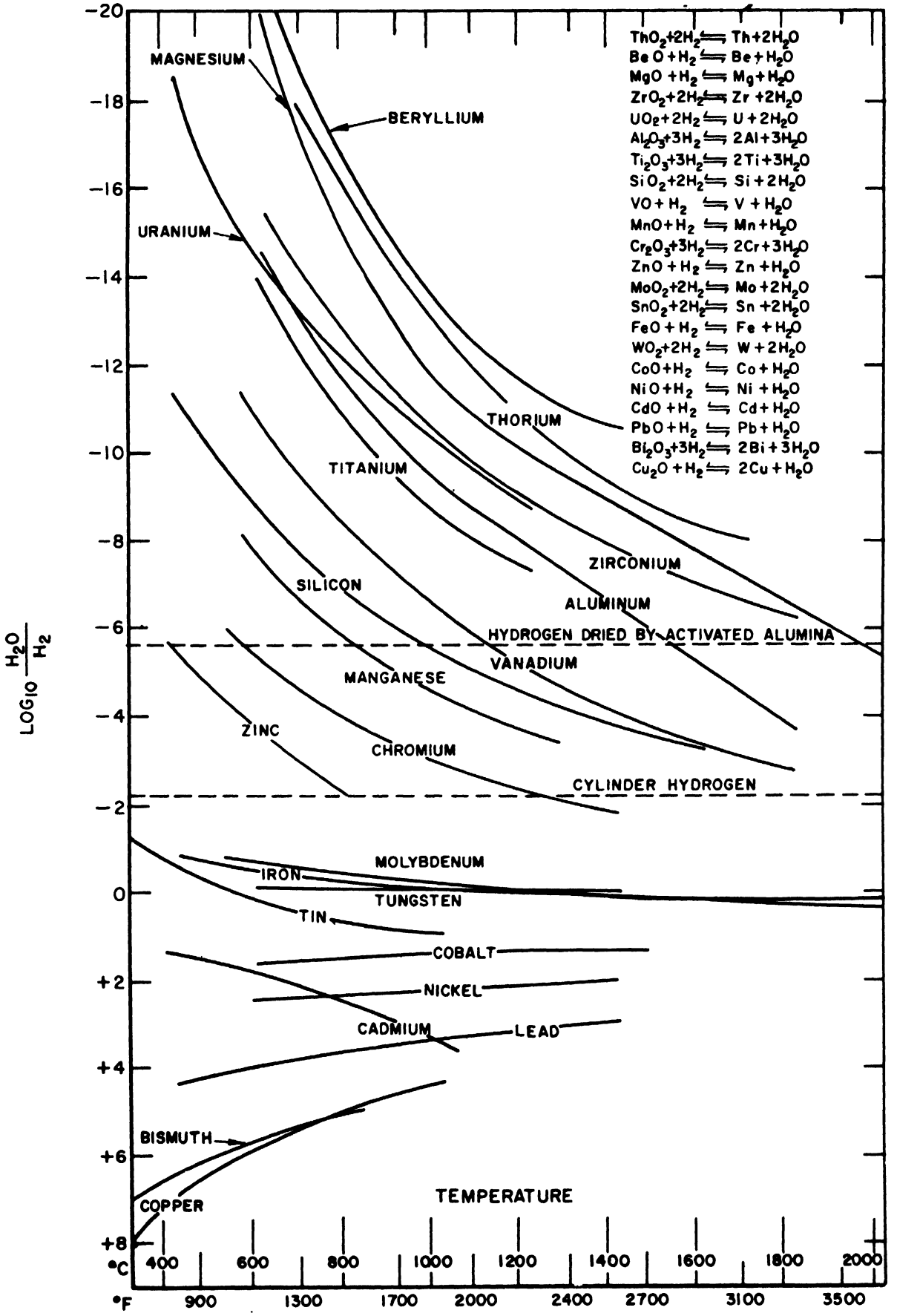

Figure 1. Equilibria of water vapor-hydrogen in several metal-metal oxide systems

Table I. $\Delta F°_{298}$ for Some Compounds of Thorium, Uranium and Other Elements

Oxides	$-\Delta F°_{298}$, *kcal*	*Halides*	$-\Delta F°_{298}$, *kcal*	*Nitrides and carbides*	$-\Delta F°_{298}$, *kcal*
½ ThO_2 (s)	140	⅙ UF_6 (g)	81	UN	75
½ UO_2 (s)	128	⅙ MoF_6 (g)	64	TiN	74
½ TiO_2 (s)	106	⅙ UCl_6 (s)	40	W_2N	11
½ CrO_2 (s)	65	⅙ WCl_6 (s)	12	Mo_2N	10
½ MnO_2 (s)	56	⅙ $MoCl_6$ (s)	11	⅓ U_2N_3	64
⅛ U_3O_8 (s)	107	⅕ UF_5 (s)	92	½ Mn_5N_2	24
¼ Fe_3O_4 (s)	60	⅕ UCl_5 (s)	48	¼ Th_3N_4	71
¼ Co_3O_4 (s)	44	¼ ThF_4 (s)	114	TiC	56
⅓ UO_3 (s)	94	¼ UF_4 (s)	102	UC	41
⅓ WO_3 (s)	61	¼ TiF_4 (s)	88	MnC	23
⅓ MoO_3 (s)	54	¼ CrF_4 (s)	67	MoC	3
FeO (s)	58	¼ MnF_4 (s)	52	WC	3
		¼ $ThCl_4$ (s)	69	⅓ U_2C_3	25
		¼ UCl_4 (s)	58	½ ThC_2	25
		¼ $TiCl_4$ (s)	42	½ UC_2	19
		¼ $MoCl_4$ (s)	15	½ Cr_3C_2	11
		¼ WCl_4 (s)	12		
		¼ UBr_4 (s)	47		
		¼ UI_4 (s)	32		
		⅓ UF_3 (s)	107		
		⅓ CrF_3 (s)	84		
		⅓ FeF_3 (s)	72		
		⅓ $ThCl_3$ (s)	76		
		⅓ UCl_3 (s)	65		
		⅓ $CrCl_3$ (s)	39		
		⅓ $MnCl_3$ (s)	32		
		⅓ UBr_3 (s)	55		
		⅓ UI_3 (s)	38		

least, drastically reduced because of the present high cost of this metal. Based upon present prices the material cost of reductant used in the case of calcium would be increased by a factor of six over the cost of magnesium. Recently, however, it appears that a method for producing high grade calcium metal aluminothermically has been developed which would help to lower future costs considerably.

The possibility of using magnesium to reduce the oxide, however, should not be dismissed lightly because of unfavorable free energies. Segregation ocurring during reduction and producing a metallic phase plus an oxide slag would alter considerably the equilibrating forces present because of the heterogeneous nature of the system, and an efficient process based upon this reaction may be entirely feasible.

Reduction processes utilizing either calcium or magnesium as the reductant can be made to yield either powder or a metallic button as the final product depending upon the amount of heat liberated during the reaction, and the fluidity and melting point of the slag product. If massive metal is desired, a low melting point slag is most advantageous since lower temperatures can be tolerated before the viscosity of the slag increases to the point where segregation of metal and slag is virtually halted. In this way, the effects of heat loss upon metal-slag separation are minimized somewhat. If, coupled with a low

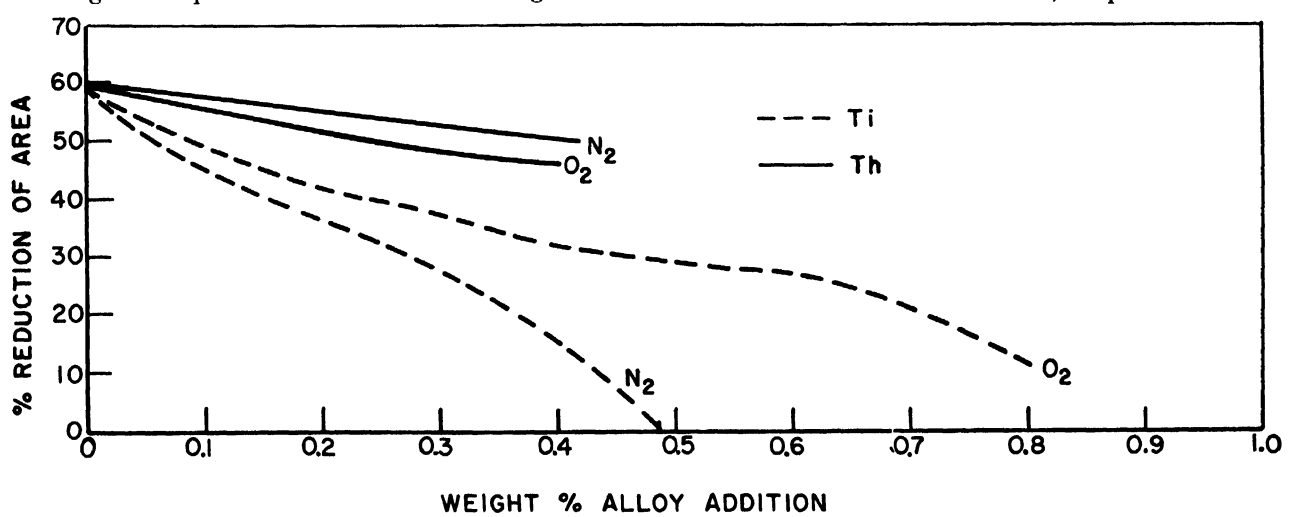

Figure 2. Effect of oxygen and nitrogen on mechanical properties of thorium and titanium

Table II. Reduction of Thorium and Uranium Compounds by Hydrogen

Reaction	$-\Delta F_{298}$, kcal	$-\Delta F_{1000}$, kcal	$-\Delta F_{2500}$, kcal
$UO_2 + 2H_2 \leftrightharpoons U + 2\ H_2O$	138	126	106
$UF_4 + 2H_2 \leftrightharpoons U + 4\ HF$	162	110	35
$UCl_4 + 2H_2 \leftrightharpoons U + 4\ HCl$	139	90	47
$ThO_2 + 2H_2 \leftrightharpoons Th + 2\ H_2O$	171	159	136
$ThF_4 + 2H_2 \leftrightharpoons Th + 4\ HF$	195	140	69
$ThCl_4 + 2H_2 \leftrightharpoons Th + 4\ HCl$	185	127	87

Table III. Reduction of Thorium and Uranium Compounds by Active Metals

Reaction	ΔF_{298}, kcal	ΔF_{1000}, kcal	ΔF_{2500}, kcal
$UO_3 + 6\ Na \leftrightharpoons U + 3\ Na_2O$	− 254	− 151	
$UO_3 + 3\ Ca \leftrightharpoons U + 3\ CaO$	− 146	− 151	
$UO_3 + 3\ Mg \leftrightharpoons U + 3\ MgO$	− 122	− 115	
$UO_2 + 4\ Na \leftrightharpoons U + 2\ Na_2O$	+ 67	+ 87	+ 207
$UO_2 + 2\ Ca \leftrightharpoons U + 2\ CaO$	−41	− 44	− 2
$UO_2 + 2\ Mg \leftrightharpoons U + 2\ MgO$	− 25	− 20	+ 47
$ThO_2 + 4\ Na \leftrightharpoons Th + 2\ Na_2O$	+ 100	+ 120	+ 237
$ThO_2 + 2\ Ca \leftrightharpoons Th + 2\ CaO$	− 8	− 11	+ 28
$ThO_2 + 2\ Mg \leftrightharpoons Th + 2\ MgO$	+ 8	+ 13	+ 77
$UF_4 + 2\ Ca \leftrightharpoons U + 2\ CaF_2$	− 135	− 127	− 72
$UF_4 + 2\ Mg \leftrightharpoons U + 2\ MgF_2$	− 79	− 69	− 10
$ThF_4 + 2\ Ca \leftrightharpoons Th + 2\ CaF_2$	− 102	− 97	− 41
$ThF_4 + 2\ Mg \leftrightharpoons Th + 2\ MgF_2$	− 46	− 39	+ 41
$UCl_4 + 2\ Ca \leftrightharpoons U + 2\ CaF_2$	− 130	− 126	− 79
$UCl_4 + 2\ Mg \leftrightharpoons U + 2\ MgF_2$	− 52	− 44	− 12
$ThCl_4 + 2\ Ca \leftrightharpoons Th + 2\ CaF_2$	− 84	− 89	− 39
$ThCl_4 + 2\ Mg \leftrightharpoons Th + 2\ MgF_2$	− 6	− 7	+ 52
$ZrO_2 + 2\ Ca \leftrightharpoons Zr + 2\ CaO$	− 40	− 46	− 7

melting slag product, the reaction is also accompanied by the liberation of a great amount of heat, the increased fluidity of the reaction products enables the reduced molten metal to separate easily so that a metallic button free of slag inclusions can be recovered. As can be seen from Table III and Table IV, reduction of the halides is more amenable to the formation of massive metal than processes involving the reduction of the oxides since these reactions are somewhat more exothermic and produce a lower melting slag. These considerations, however, are more applicable to uranium reduction because of its lower melting point. The preparation of pure thorium metal in massive form directly during reduction is considerably more difficult. It is unlikely that refractory materials capable of withstanding attack at 1800°C, the melting point of thorium, can be found. In this case, therefore, it would probably be more advantageous to produce a powder which could subsequently be arc-melted with consumable thorium electrodes, using a water-cooled hearth.

In addition, the possible formation of intermediate compounds between the starting material and the reaction product, such as Na_2UO_4 should not be overlooked in evaluating the behavior of various reactions. Some of these have been found to be fairly stable, and failure to account for their formation will lead to erroneous conclusions regarding the efficiency of the reaction in question.

REDUCTION BY CARBON

Both thorium and uranium oxides have unfavorable free energies in their reaction with carbon. This is counterbalanced by the formation of a gaseous reaction product which can be continuously removed by vacuum, thereby upsetting the equilibrium. Both reactions have been studied to determine the equilibrium gas pressure over a wide temperature range and these data appear plotted in Fig. 3, together with the equilibrium pressure observed in the ZrO_2-C and TiO_2-C systems for comparison.[2-5] From a study of this plot, it is obvious that for the two metals of interest, fairly high temperatures are required to obtain carbon monoxide pressures capable of being removed by conventional pumping equipment in a reasonable length of time. For instance, at 1700°C, the equilibrium carbon monoxide pressure in a UO_2-C system is in the range of 250 mm, but in the case of ThO_2-C it is considerably less. To date, no refractory material has been found which is inert to these metals at the operating temperatures required for reduction. These range around 2200°C and therefore it has become necessary to conduct these reactions in graphite crucibles. Because of this, however, contamination of the molten metal with excess carbon invariably occurs.

Of considerable interest in this connection are the phase diagrams for both the uranium-carbon[6] and the thorium-carbon[7] systems. As can be seen in Fig. 4 and Fig. 5, respectively, the uranium-carbon system is the more favorable for the production of pure metal since carbon is virtually insoluble in uranium up to a composition of 50 atomic percent. This implies that a melt containing, say, 2 or 3% excess carbon, as might be found at the end of a reduction due to contamination from the graphite crucible, would, upon solidification, appear as a mixture of essentially pure uranium metal and uranium carbide. There are indications that methods of separating the carbide phase from the uranium phase may be successful.

Table IV. Melting Point of Slag Products

$CaCl_2$	782°C
CaF_2	1418
CaO	2600
$MgCl_2$	714
MgF_2	1263
MgO	2900

Table V. Carbide-Oxide Product

Carbide	*Oxide*	*Product*
0.098	0.028	0.002744
0.087	0.028	0.002436
0.56	0.006	0.00336
0.19	0.07	0.0133
0.29	0.178	0.05162
0.09	0.037	0.00333

This segregation does not occur in the thorium-carbon system since a solid solution is formed over an appreciable concentration range immediately upon freezing. Although the solid solution phase is unstable at lower temperatures and can be decomposed into two phases by very long-time annealing (solid-solid reactions are very sluggish), the final reaction products are still a mixture of thorium-carbon solid solution and thorium carbide, rather than pure metal and carbide phases as can be obtained with uranium melts. As shown in Fig. 6, carbon has an adverse effect upon the mechanical properties of thorium. This is reflected in the sharp decrease in per cent reduction in area with increasing carbon content. Thus reduction of thorium oxide by carbon cannot produce good grade metal having suitable mechanical properties. This has been verified experimentally.

The difference in the two reactions, i.e., UO_2-C and ThO_2-C, becomes quite clear when photomicrographs of the final product obtained in each case are compared. In the case of the U-C reaction, it can be seen from Fig. 7 that the two products, metal and carbide, are completely segregated into two separate and distinct phases. This has not occurred in the Th-C system, Fig. 8. In this case, partial decomposition of the original solid solution into a carbon-rich and a carbon-poor phase occurring as a solid-solid reaction has produced an intimate mixture of products quite unlike that formed with the U-C melt.

Further, in the case of uranium, studies have been made of the reaction between uranium oxide-uranium carbide mixtures which have been arc melted to obtain the high temperatures required for reduction. To prevent contamination of the melt by excess carbon from the container, a water-cooled copper hearth and tungsten-tipped electrodes were used. It is interesting to note that metal simultaneously low in both oxygen and carbon has not yet been produced under the conditions employed. As a matter of fact, the product of the oxygen and carbon content appears in many instances to be relatively constant, though only limited data, shown in Table V, have been collected. It seems likely, however, that more prolonged heating times or higher temperatures would result in a smaller oxygen-carbon "constant".

DIRECT PREPARATION OF POWDERED METAL

Because of the relatively high melting point of these metals, particularly thorium, the metal product

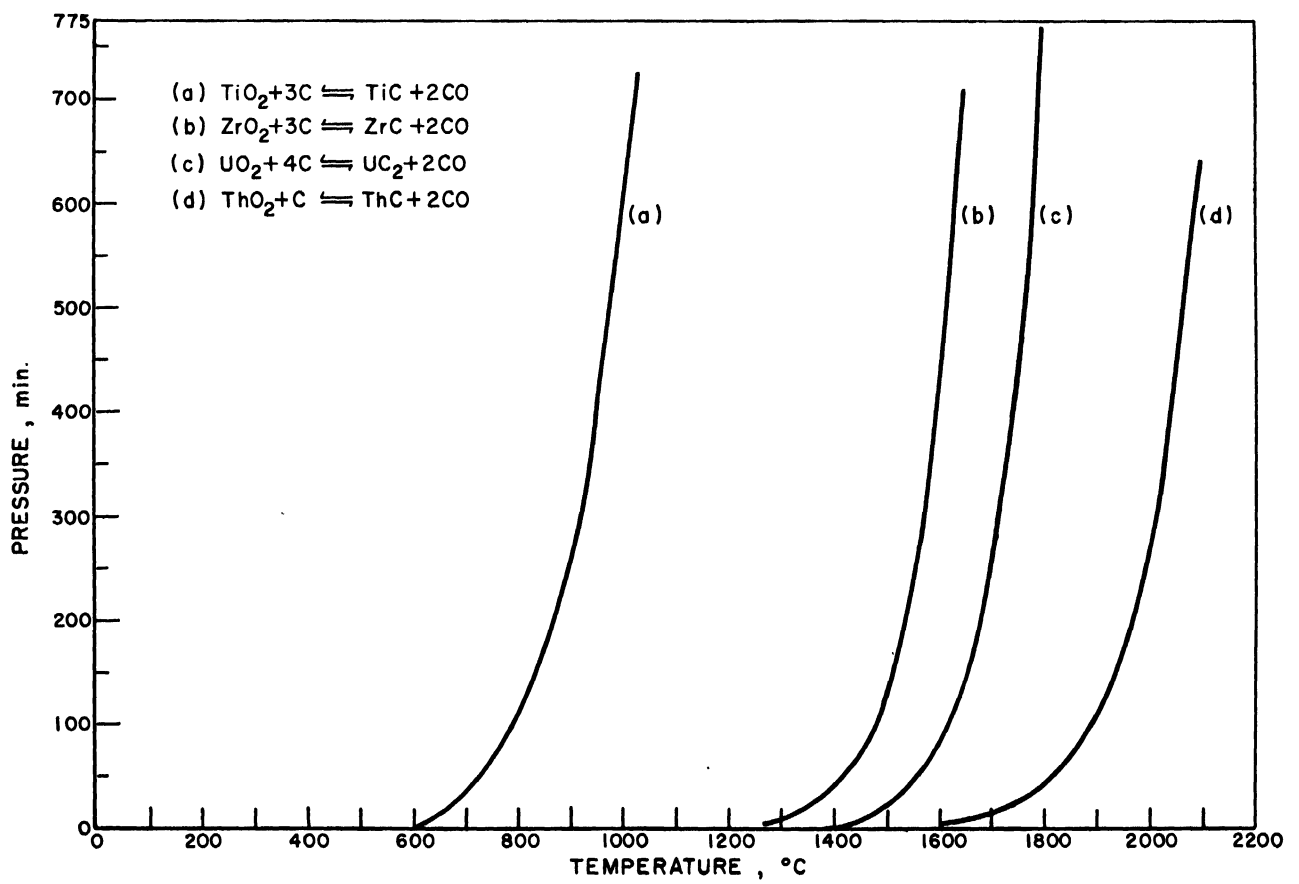

Figure 3. Carbon monoxide equilibrium pressures

obtained by various processes is often in the form of a powder rather than massive, reguline metal. Although this may present some advantages if powder metallurgical techniques are to be employed for fabrication, it is also associated with certain difficulties. In every case, the powdered product is found intimately associated with slag from which it must be completely separated either chemically or by mechanical means. In general, mechanical methods do not give adequate separations and chemical methods such as hydriding or leaching with water or dilute acids become necessary. These latter methods, as for instance the leaching of powder by dilute acetic acid, often result in the formation of a layer of oxide on each particle if allowed to remain too long in contact with an aqueous solution or if careful control over the temperature is not exercised. Also, very fine particles are quite often lost by dissolution, thus adversely affecting the yields.

Because of the large surface area per unit weight of metal in very fine powder, contamination by the atmosphere proceeds very rapidly if the product is left exposed and, in some cases, may ignite the powder spontaneously. This pyrophoricity, which is characteristic of some of these metal powders as well as compounds such as their hydrides, presents a definite hazard and special techniques are required to handle these materials. Perhaps the simplest of these methods involves the use of a non-reactive liquid of low boiling point under which these powders can be collected. Non-polar organic liquids such as naphtha, benzene or hexane, have been found particularly suitable. Another successful technique is based upon the use of protective coatings on the individual powdered particles such as a low melting wax, or plastics or resins dissolved in a suitable solvent. Materials so treated can then be safely stored or handled without fear of self-ignition.

Neither of these methods, however, may be suitable under certain circumstances, and in these cases the use of an inert atmosphere as a protective blanket becomes necessary. In most cases nitrogen or argon, dried by activated alumina and deoxidized by hot copper, offers adequate protection. Air-tight containers through which the protective inert gas is allowed to flow and which are equipped with

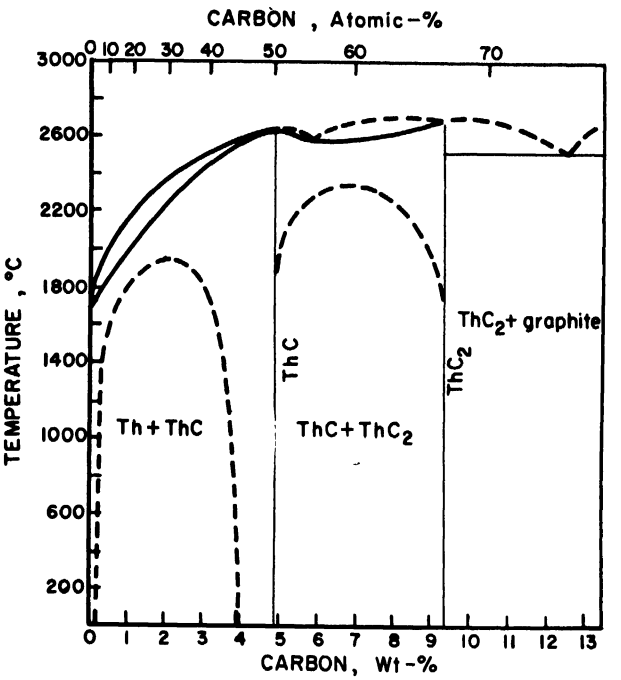

Figure 5. Thorium-carbon system

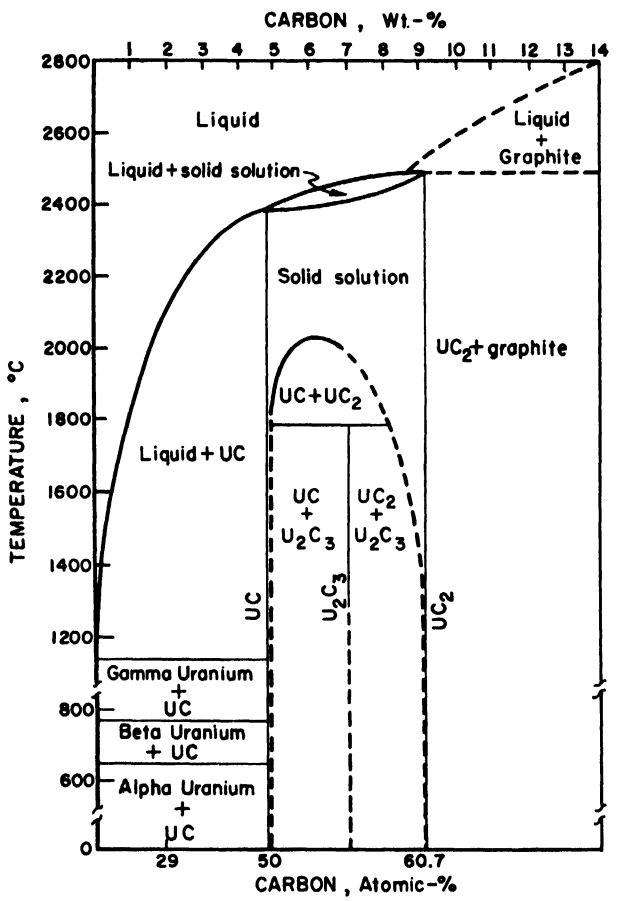

Figure 4. Uranium-carbon system

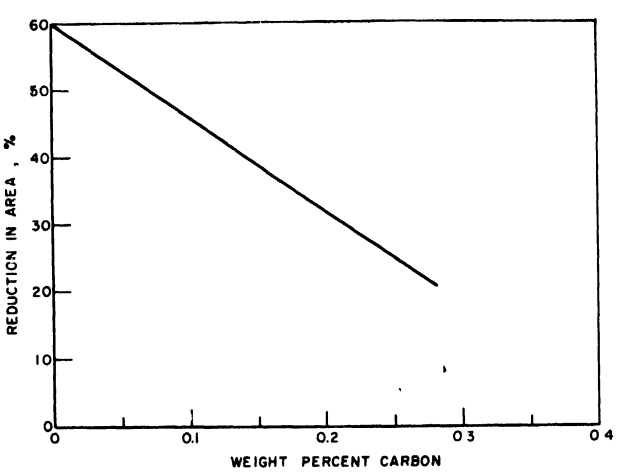

Figure 6. Effect of carbon on the mechanical properties of thorium

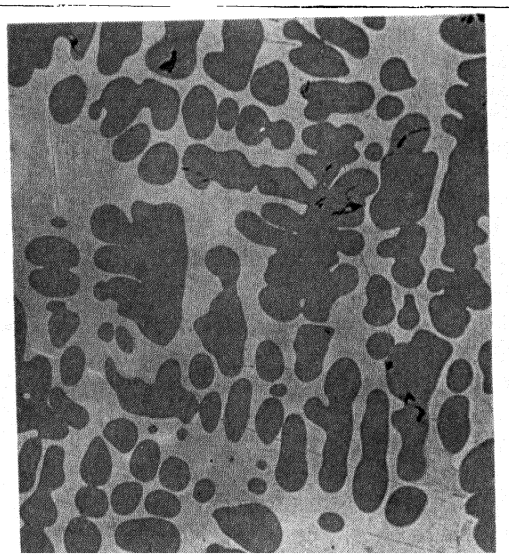

Figure 7. Photomicrograph showing product obtained from carbon reduction of uranium dioxide

sealed-in rubber gloves, have also been found convenient for handling these pyrophoric metals.

Since pyrophoricity is intimately associated with the particle size and shape of metals, control of these variables in any reduction process yielding powder as a product becomes an important consideration. As a general rule pyrophoricity is most frequently found to occur with partially sintered agglomerate particles having a porous surface, as well as with very fine powders. It is interesting to note that the tendency to ignite spontaneously in air is considerably increased when these powders are not thoroughly dried. A moisture content of approximately 5% appears to be the most critical in this respect.

Partially sintered agglomerates usually form when reduction takes place at a temperature below the melting point of the metal product, i.e., 1133°C for uranium and 1827°C for thorium. The appearance of these particles is believed due to a mass of small individual particles which because of their high melting point sinter without coalescing into larger spheres. An example of this type of reaction can be had by comparing the nature of the powder produced by the calcium reduction of uranium dioxide in the presence of a calcium chloride flux to that formed when zirconium dioxide is similarly reduced. In the case of uranium this process, as originally described by Marden[8] and by Cachemaille[9], produced non-pyrophoric powder, minus 200 mesh (approximately 75 microns) in size. More recently, a similar process was adopted in Germany during the last war to produce uranium powder at Begussa. Powder was produced of which 20–30% included particles larger than 70 microns.

If this process, with a similar furnace temperature (about 1100°C), is applied to the reduction of zirconium oxide, however, a highly pyrophoric powder having an average particle size of 3 to 4 microns is produced. A typical particle size distribution curve

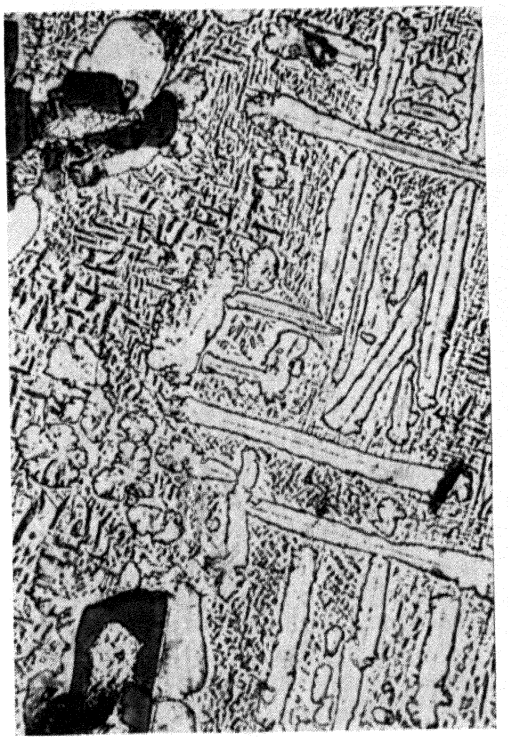

Figure 8. Photomicrograph showing product obtained from carbon reduction of thorium dioxide

of this powder is shown in Fig. 9. From this it can be seen that the largest weight fraction of the zirconium powder is less than two microns in size. Both reactions have approximately the same free energy change (Table III), the same heat balance, and the same slag product. Thus it can be assumed that the sharp difference in the nature of the two powders produced is due solely to the higher melting point of zirconium (1700°C) which prevents coalescence of the particles. In the case of uranium, however, the reaction temperature reached during

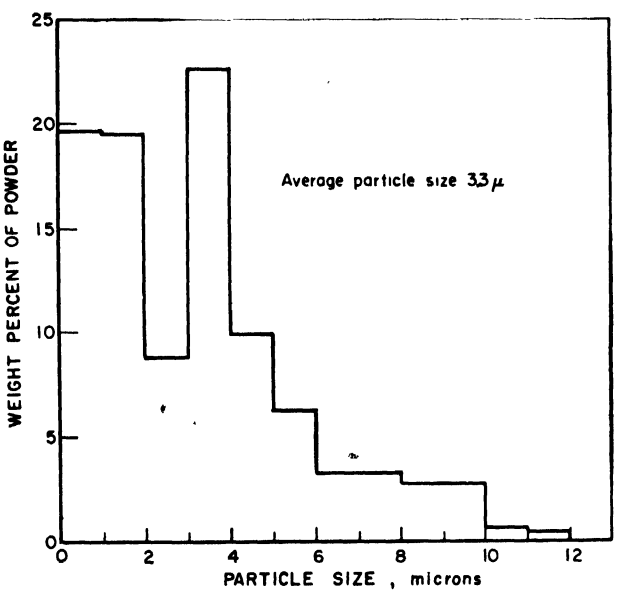

Figure 9. Particle size distribution for calcium reduced zirconium oxide

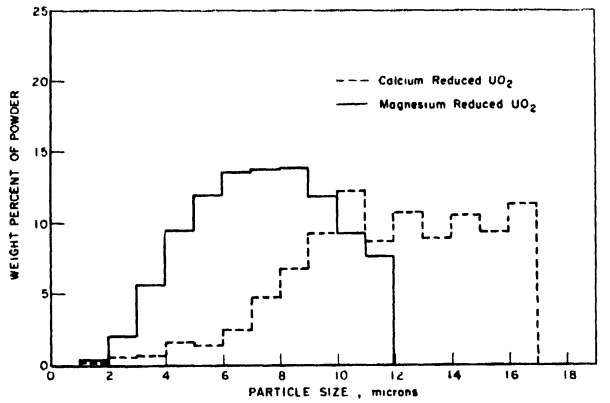

Figure 10. Particle size distribution of uranium metal

reduction exceeds the melting point of the metal. The individual particles fuse and tend to coalesce into larger spheres that are usually non-pyrophoric.

Another example of the effect upon the particle size of the amount of heat evolved during reduction can be had by comparing the powder produced when (1) uranium dioxide is reduced by calcium in the absence of a flux; and (2) uranium dioxide is reduced by magnesium in the presence of magnesium chloride. In the latter case, because the reaction is not as highly exothermic, less heat is available so that growth of the metal particles is inhibited. Particle size distribution curves for powders prepared by both methods appear in Fig. 10.

As can be seen, the size and nature of the particles produced depend largely upon the peak temperature obtained in the reaction, upon the melting point and fluidity of the slag produced, and upon the rate of heat loss from the reaction products. The melting point of the slag formed during a reduction process can be varied within certain limits by including various fluxing agents in the charge. This practice, however, lowers somewhat the peak temperatures reached during reduction because of absorption of some of the heat of reaction. A fairly reliable estimate of the maximum temperatures reached can be had by computing the heat and material balance for a particular system, assuming practically adiabatic conditions, i.e., a small but fixed heat loss to the environment. In actual pratice the quantity of heat lost depends upon the scale of the operation. This method, however, affords a convenient means of comparing various processes with respect to the type of product which may be expected.

THE PREPARATION OF METAL POWDERS BY HYDRIDING

Because of economic considerations as well as the requirements of particular applications, it may sometimes be necessary to comminute massive thorium or uranium. Due to ductility neither thorium nor uranium can be converted to powder by ordinary mechanical methods when pure. Their hydrides, howby heating the metals under a hydrogen atmosphere, ever, are quite brittle. These are easily prepared a temperature of approximately 225°C being required to form UH_3 and 700°C for ThH_2. In the case of uranium, the hydride converts directly to powder, whereas thorium hydride forms a sinter-cake which must be pulverized mechanically. Both hydrides are then decomposed under vacuum (550–600°C in the case of uranium and 750°C for thorium) and reconverted to metal. Again in the case of thorium, a sinter-cake is formed which powders upon grinding. Fine metal particles, highly pyrophoric in nature, are obtained in each case. Particle size distribution curves are presented in Fig. 11 for thorium powder and thorium hydride, and in Fig. 12 for uranium powder and uranium hydride. As can be seen from these curves, both hydride powders have extremely fine particle sizes. These fine sizes, however, cannot be retained during decomposition to metal because of sintering which inevitably occurs.

In comparing the size distribution curves for powders produced by different processes, the method used in particle size analysis must be kept in mind. For instance, powders analyzed by microscopic counting generally result in much smaller particle size readings in comparison to results obtained by turbidometric or gas pressure drop methods. This may be due largely to a tendency to interpret sintered

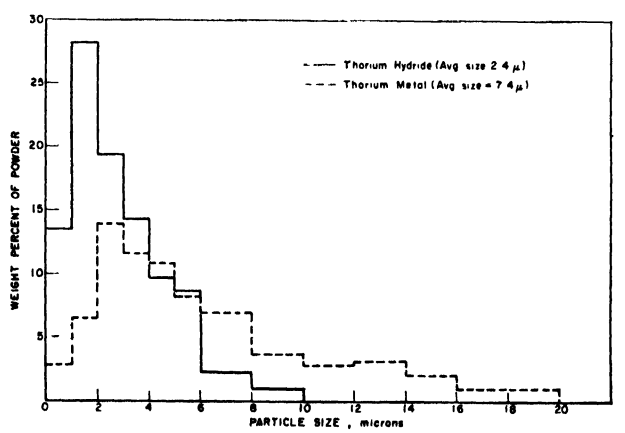

Figure 11. Particle size distribution curve for calcium reduced thorium and Th-hydride

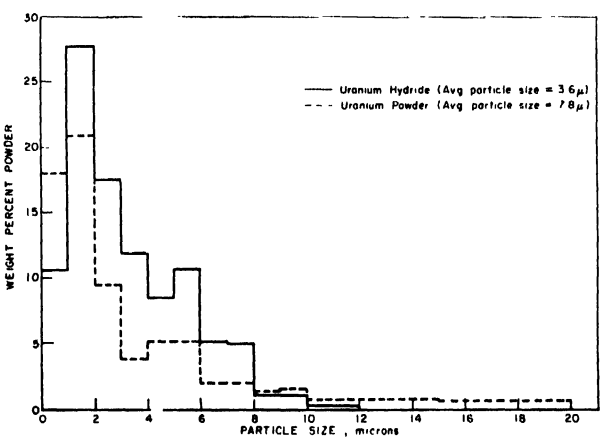
Uranium Hydride (Avg particle size = 3.6 μ)
Uranium Powder (Avg particle size = 7.8 μ)
WEIGHT PERCENT POWDER
PARTICLE SIZE , microns

Figure 12. Particle size distribution of uranium and uranium hydride

agglomerates as being composed of individual particles when measured under a microscope. In methods of analysis based on Stoke's Law, however, these agglomerates act as single particles and a larger average particle size is obtained. Thus, since the size distribution curves of the powders shown in Fig. 10 were obtained by microscopic counting, whereas those in Fig. 9, 11 and 12 were determined turbidometrically, a direct comparison of these data may lead to erroneous conclusions and should be avoided.

CONCLUSION

Various methods useful for the production of thorium and uranium metal have been examined from the standpoint of ease of reduction, cost and purity of the product, as well as the type of product which will be produced, i.e., powder or a solid regulus. The advantages of each process depend largely upon the over-all cost of producing the metal as well as the use to which these metals will be put. As an example, uranium metal which is to be used as cast or which will require a minimum amount of working may tolerate more impurities than metal which must be subjected to severe deformation.

Although the methods used for the production of thorium and uranium are basically similar, essential differences are evident because of the higher melting point of thorium. Uranium metal can easily be prepared either as powder or directly in massive form. Thorium metal however, because of its higher melting point, presents much greater contamination problems when prepared in the massive state. In this case the production of a powder which could be consolidated by arc melting, using consumable electrodes, would undoubtedly be a more advantageous approach.

Carbon reduction for both uranium oxide and thorium oxide has been considered. It has been shown that there is a possibility of producing pure uranium by this method whereas only carbide or solid solution forms with thorium, due to the inevitable contamination from the graphite container.

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Metallurgy of Thorium

By G. E. Kaplan, USSR

Thorium as well as uranium is used for production of atomic energy. High purity of thorium with regard to elements with a large cross section of neutron absorption is the main requirement for thorium used for the purpose.

Monazite concentrate is used for obtaining thorium. However, it is not the only source of thorium. Methods are developed permitting the extraction of thorium as a secondary product from certain types of polymetallic ores.

Natural sands containing monazite are concentrated by usual methods of gravitation and magnetic separation to obtain monazite concentrate, which has to be subjected to chemical treatment.

The technology of thorium production from monazite includes obtaining thorium solution, its separation from impurities, production of pure thorium compounds and reduction of the metal from these compounds.

Much attention was paid to the development of a suitable method of decomposing monazite concentrate to obtain thorium and rare earth elements in a soluble form. Various technological methods were studied, much attention being paid to acid and alkali ones.[1, 2]

The well known method of sulphation of the concentrate at the temperature of 200–300° was studied in detail. A rotating sulphator with automatic feeding of sulphuric acid and the concentrate as well as with an automatic discharge of the product obtained was used to secure continuity of the process, to increase productivity and improve working conditions. The design of the sulphator provided for a practically complete absorption of the sulphuric acid vapours by means of electric filters.

There were also developed industrial alkali methods for concentrate decomposition. They included treatment of the concentrate with caustic soda solution, or fusing with caustic soda, or roasting with sodium carbonate.

The first steps of treating the products of both acid and alkaline decomposition do not present any considerable difficulty and result, as a rule, in obtaining a mixture of thorium and rare earth compounds on separation from phosphoric and sulphuric acids.

A method of separation of Th and rare earths as fluorides or double sulphates was used for treating the products of acid decomposition of the concentrate. The separation was accompanied by production of sulphophosphoric acid solution, which may be used for the manufacture of simple type fertilizers. A method was developed for treating the products of alkaline decomposition of the concentrate to secure the production of thorium and rare earth hydroxides with simultaneous separation of trisodiumphosphate. During the subsequent dissolving of hydroxides in the acid, fluoride ion was added under established conditions to secure complete solution of thorium and the rare earth elements.

The most important and complicated problem is the further separation of thorium and rare earth elements. The importance of this problem lies in the fact that the rare earth elements which are present in large amounts in almost all types of thorium raw materials are very closely related to thorium with respect to their properties. This necessitated the study of a number of processes based on the utilization of slight differences in properties of thorium and rare earth compounds.

The following most important methods were studied, developed and improved:

(*a*) Methods based on the difference between the hydrolytic properties of thorium and those of the rare earth elements. The main point of these methods is to separate hydroxides, phosphates and other compounds of these elements using different concentrations of hydrogen ions. There were used processes of thorium hydroxide precipitation from solution by partial neutralization as well as methods based on the preferential dissolution of rare earth elements during the acid treatment of mixtures of their hydroxides and thorium hydroxide or mixtures of phosphates, until a certain value of ion concentration is reached. The use of these methods made it possible to obtain half-way products with the ratio between thorium and rare earth elements of 10 to 1 instead of the average ratio of 1 to 10 in raw materials.

(*b*) The processes based on the difference in solubility of some salts of thorium and rare earth elements. A detailed study of a number of methods showed that the best results may be obtained when thorium is separated from acid solutions as oxalate and sulphate, the maximum refining being reached by sulphate crystallization. The sulphate crystallization is necessary to obtain thorium compounds of high purity which are the final products (e.g., thorium oxide). At the same time the precipitation of oxalate is quite sufficient to purify thorium from rare earth elements with the purpose of subsequent

Original language: Russian.

production of thorium fluoride and metallic thorium by the electrolysis of fused fluoride. During the electrolysis some additional refining of the metal takes place and therefore the requirements for the purity of the original chemical compounds may be somewhat relaxed.

(*c*) Methods of separation of the rare earth elements from thorium to obtain a product with a very high degree of purity based on the use of special sorbents.

(*d*) An extraction method from nitric acid solutions by means of various reagents: tributyl-phosphate and other phosphoric acid ethers.

By using these methods it is possible to obtain thorium compounds of any desired degree of purity both from monazite concentrate and from polymetallic ores.

Several methods were investigated to obtain metallic thorium: (1) electrolysis of fused salts with a liquid cathode; (2) electrolysis of fused salts with a solid cathode; (3) calcium reduction method.

All these methods result in obtaining thorium powder. The electrolysis of fused thorium fluoride mixture with potassium and sodium chlorides with a solid cathode is carried out on the large scale. This method ensures sufficiently effective additional removal of impurities.

The amount of rare earth impurities in thorium is decreased many times during electrolysis. The cathode product is a mixture of thorium metal crystals with the solidified electrolyte.

The cathode rods are of good electric conductivity and may be elongated up to one meter. During the process of electrolysis a mechanical device is used for squeezing the cathode rods to remove excess of the electrolyte picked up.

The mechanism of the electrolysis and physicochemical properties of the electrolyte were studied in detail. The research made it possible to throw light upon the nature of the processes that take place in the electrolytic bath and to choose correct technological conditions.

Equilibrium diagrams of the following systems: ThF_4-NaCl, ThF_4-KCl, ThF_4-NaF, ThF_4-KF, NaCl-KCl-ThF_4, NaF-KF-ThF_4 and others were investigated to study the composition and physicochemical properties of the electrolyte.

Examples of such diagrams are shown on Figs. 1, 2, 3.

X-ray as well as chemical analysis of the electrolyte contributed to the thorough examination of the nature of the phenomena taking place during the electrolysis. From these analyses it is concluded that dissociation of the thorium fluoride occurs in the electrolyte. It is established that fluoride complexes are formed in the electrolyte. Their dissociation is effected stepwise and as a result of this thorium may be present in the bath both in anionic and cationic forms.

Anodic processes were also studied. Compositions of anodic gases and their change with variation in electrolysis conditions were studied in baths with an insoluble anode. Preferential discharge of elementary chlorine at the anode is characteristic of the electrolysis process with graphite anode. A partial discharge of fluorine at the anode both in elementary

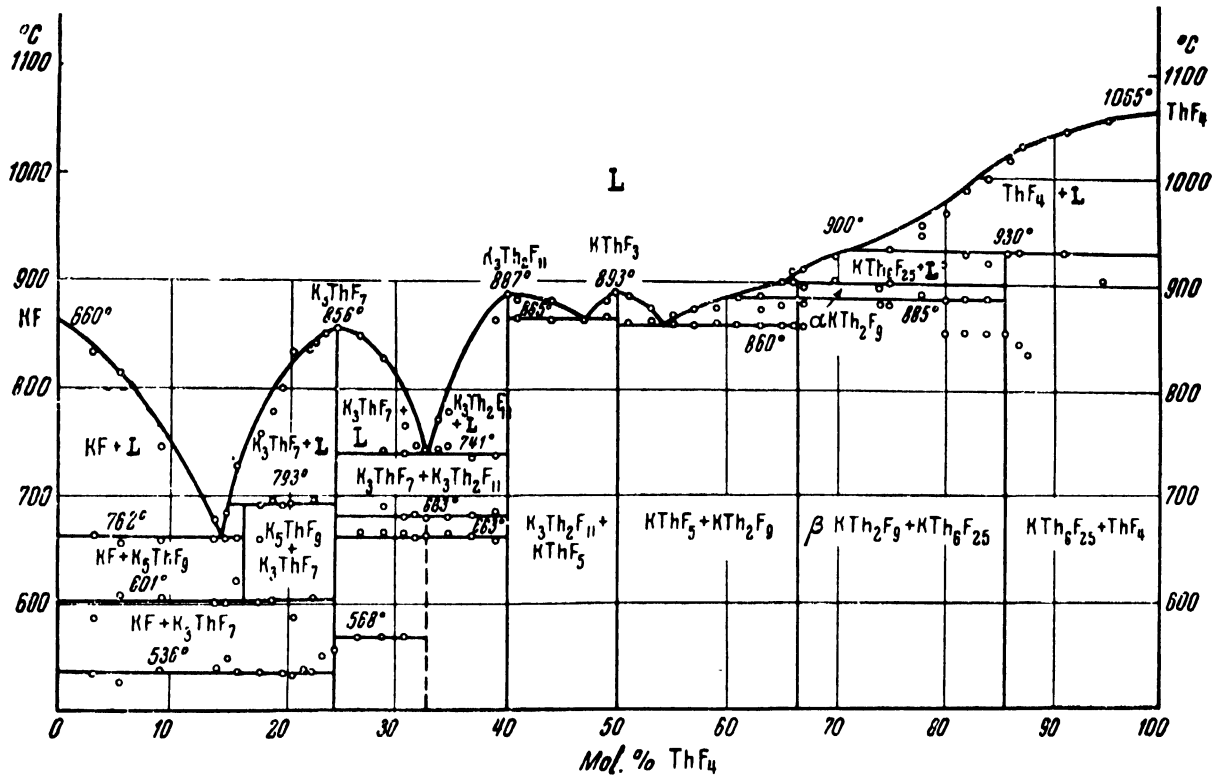

Figure 1. Equilibrium diagram of KF-ThF_4 system

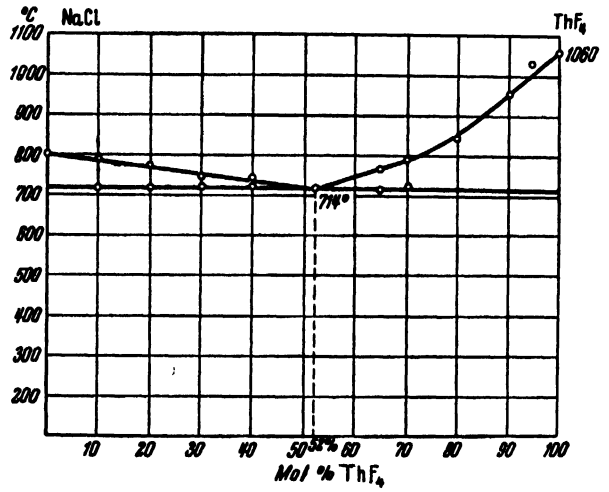

Figure 3. Equilibrium diagram of NaCl-ThF_4 system

form and in the form of a carbon compound also takes place during the process of electrolysis. Accumulation of F^- in the electrolyte gives rise to an anodic effect which occurs periodically in the bath. The composition of the electrolyte, temperature, and kind of anode graphite influence the anodic effect. As a result of a detailed study of these factors, measures were elaborated preventing the occurrence of the anodic effect.

A study of electrolysis conditions (temperature of the electrolyte and its composition, cathode and anode current density) contributed to the establishment of process conditions that ensure obtaining a metal powder of the optimum grain-size.

It was established that if cathodic current density is less than 4 amp/dcm² the metal is obtained in the form of such a fine powder that it passes nearly completely into the slurry during the subsequent concentration by gravity. If the current density is about 20 amp/dcm² it is possible get a stable metal yield as well as current efficiency of the order of 70–80%.

The influence of the electrolyte temperature was studied in the range of 500 to 1000°. At low temperatures of the order of 500° current efficiency and metal yield are very small and the powder obtained is not suitable for concentration operations. A rise of a temperature up to 800° makes it possible to increase current efficiency and metal yield up to 70–80%, and to obtain a powder of the optimum particle-size permitting its use directly for production of the compact metal by powder metallurgy methods. Further rise of the temperature of the bath brings about a decrease of current efficiency and metal yield and an increased content of fine fractions of the powder.

Thermal conditions of the electrolyte depend to a great extent upon volume density of current because the temperature in an industrial bath is maintained according to the emission of Joulean heat. It was established that a current density of 60–70 amp/kg of electrolyte is necessary to maintain the optimum temperature.

The critical value of the anode current density proved to be 0.5 amp/dcm². It was observed that a high anode current density results in the appearance of intensive convection currents that carry anodic products to the cathode, thus contributing to the dissolving of precipitated thorium crystals.

Also studied was the effect of changes in the concentration of thorium fluoride in the electrolyte on current efficiency and on the yield of the metal. It was established that decrease in thorium content of the bath below 11% (by weight) results in a discharge of alkali metal ions at the cathode. If the concentration of thorium in the electrolyte is high enough continuous electrolysis without an appreci-

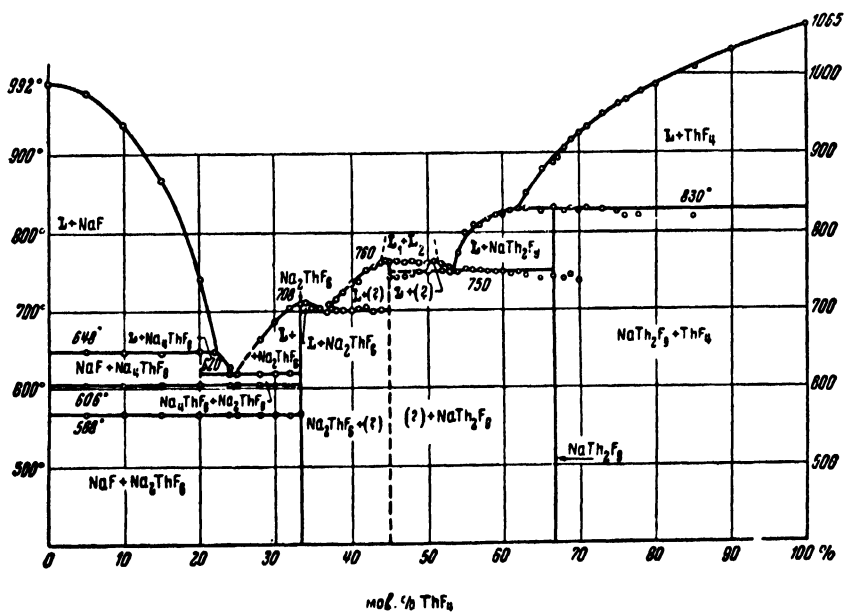

Figure 2. Equilibrium diagram of NaF-ThF_4 system

able discharge of alkali metals is possible. A bath with a thorium concentration in the electrolyte of more than 11% can operate for a long period of time because sodium and potassium fluorides formed during the process of the electrolysis are removed from it together with the cathode product. Thus, the electrolyte in the bath is practically renewed after a certain period of time, however the use of excessively high thorium concentrations in the electrolyte results in picking up electrolyte rich in thorium salts by cathode rods.

In studying thorium electrolysis considerable attention was paid to the quality of the original raw materials and the behaviour of the impurities. The appearance of rare earth elements, zirconium and hafnium in thorium fluoride is due to their presence in monazite. The main reason for the presence of such impurities as iron, manganese, chromium, nickel, copper and boron lies in the corrosion of the equipment. As might be expected, the impurities which are electrically more positive than thorium (zirconium, iron, copper, nickel, manganese) are practically completely deposited at cathode and make the metal impure. The decomposition voltage of rare earth elements is higher than that of thorium fluoride and therefore they do not pass onto cathode metal but accumulate in the electrolyte. Comparatively low concentration of rare earth elements in the electrolyte also contributes to this. The deleterious influence of sulphur and phosphorus on the process of electrolysis was also established and therefore their content in the fluoride should be reduced to a minimum. Considerable attention is being paid to thorough dehydration of thorium fluoride because traces of water render the process inoperable.

An electrolysis bath operates continuously until complete depreciation of the lining. The cathode rod raised from the bath contains approximately 50% (by weight) of the electrolyte, however the easiness of extraction and regeneration of thorium fluoride which are carried out by elementary operations makes the present process beneficial. Cathode rods are crushed into pieces of 10–15 mm. The pieces of the cathode product are treated with water in special vane mills. This operation is necessary for completely breaking the joints of metal crystals with electrolyte particles and the removal of soluble components of the latter. The pulp from the vane mill passes through a series of hydraulic separators. Large conglomerates of metal crystals and unbroken joints are separated by this operation. After passing through the separators the pulp is delivered onto concentration tables. Three products are obtained on the table: thorium powder free from electrolyte particles, half-way product that may be put in the process again, and a slurry containing the insoluble part of electrolyte with a insignificant content of fine powder fractions. Thorium powder obtained from the tables is magnetically separated to remove mechanical impurities of iron, washed with dilute nitric acid, dehydrated, dried and is converted into compact metal.

Drainage from the concentration tables is clarified in settlers, the slurry together with other by-products of the electrochemical process is delivered for chemical treatment.

Thus, in spite of comparatively low direct metal yield during electrolysis, the present process is sufficiently satisfactory due to operation in a closed cycle and the complete utilization of all by-products to make it possible to reach almost theoretical values for the overall yield of thorium from the original raw materials.

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Powder Metallurgy of Thorium

By G. A. Meyerson, USSR

Thorium used for the production of atomic energy must be of high chemical purity, and has to be ductile for manufacturing solid articles.

Pure thorium obtained by metallurgical processes is produced in the form of a powder. This fact, as well as the high melting point and chemical activity of thorium, and difficulties in the choice of an inert material for crucibles and moulds, makes methods

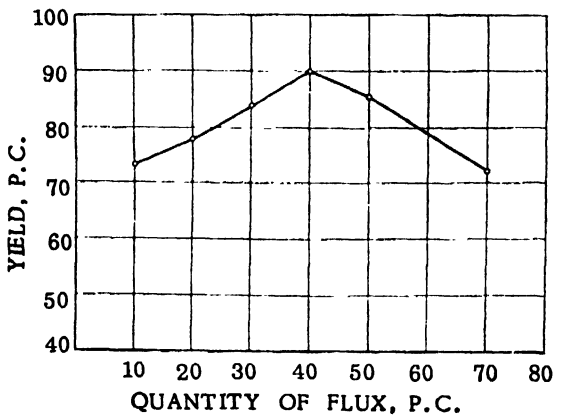

Figure 1. Influence of the amount of calcium chloride: the yield on thorium powder

of powder metallurgy the most suitable for the production of fabricated thorium bodies.

The original thorium powder may be obtained by two main methods: by electrolysis of its fused salts and by calcium reduction of thorium dioxide.

The methods of producing thorium compounds and electrolytic thorium powder of the necessary degree of purity are described in the report on thorium metallurgy, therefore this paper will be confined to the calcium reduction of thoria and the subsequent pressing and sintering of thorium powders produced by both methods.

Treatment of thorium dioxide with calcium results in complete reduction to the metal. However, the quality of the powder depends on its subsequent, inevitable partial oxidation during table concentration and washing with dilute nitric acid as well as in the process of drying. One of the main factors affecting the oxidisability of the powder is its particle size. At the same time the particle size of the calcium reduced powder essentially influences the yield of the powder after washing, since the finest fractions form into a sludge.

Original language: Russian.

As is known, the addition of calcium chloride as a flux is used to increase the particle size of high melting metal powders in the reduction of their oxides with calcium.

The quantity of calcium chloride suggested for the charge, as well as that of metallic calcium, vary over a wide range according to the data in the literature; that is why it was necessary to investigate the optimum charge composition.

Besides this, the following factors were also studied: The temperature conditions of the reduction process; the influence of atmosphere (argon, vacuum); the behaviour of the rare earths (which are the chief impurities in thorium) during reduction and the subsequent treatment of the powder.

CALCIUM REDUCTION OF THORIUM DIOXIDE

An investigation of the process of calcium reduction of thorium dioxide in an argon atmosphere with various amounts of calcium chloride established that the highest direct yield of thorium powder is obtained when 40% (of the weight of thoria) of calcium chloride is added to the charge (see Fig. 1).

A further increase in the amount of calcium chloride added dilutes the charge and deteriorates the contact between the components as well as reduces the concentration of metallic calcium dissolved in the fused calcium chloride. It results in a decrease in the yield of washed thorium powder.

The contact between reagents can be improved by briquetting the charge before feeding it to the reactor.

It has been established that an excess of 25% of metallic calcium over that required by theory is sufficient to effect complete reduction of the thorium dioxide.

The reduction process may be carried out under vacuum. However, reduction in an inert gas atmosphere is preferred, since under these conditions the evaporation of calcium from the charge is slowed down.

The temperature conditions of the reduction process were investigated over a wide range of temperatures (700–1200°). The best results as regards to the quality and yield of thorium powder were obtained at a reduction temperature of 1000 to 1100°C.

After reduction, the mixture was treated with water and dilute hydrochloric acid to dissolve calcium oxide and excess calcium followed by treatment of the powder on a concentration table. This latter process was accompanied by the separation of a

Table I

Element	Content, %	
	Calcium-reduced powder	Electrolytic powder
Thorium	99.6–99.8	99.6–99.7
Iron	0.02–0.04	0.024–0.06
Fluorine	0.02–0.05	0.20–0.40
Chlorine	0.002–0.003	0.003–0.015
Nitrogen	0.005–0.017	0.003–0.010
Sodium	0.002–0.005	0.003–0.010
Calcium	0.1–0.12	0.003

sludge consisting of the very fine, and therefore most oxidized, particles of thorium and thorium dioxide. After settling the thorium powder was purified by magnetic separation from mechanical admixtures of iron. The thorium powder obtained was washed with 15% nitric acid solution to increase its purity and dissolve the oxide films from the particles.

A study of the behaviour of boron, uranium and the rare earth elements during the reduction of the thorium oxide showed that 70–80% of these impurities (in relation to their content in the initial thorium oxide) concentrates in the thorium powder. Hence, to meet the requirements regarding these impurities the original oxide used in the production of thorium must be sufficiently pure.

The direct yield of the washed powder is about 90% in relation to the thorium content in the initial dioxide. Analysis of the calcium reduced thorium powder is given below.

WASHING THE POWDER WITH NITRIC ACID

The first experiments on the use of thorium powders washed only with water showed that such powders contained a considerable amount of impurities (up to 1–3%). These impurities in the calcium reduced powder consisted mainly of thorium dioxide, calcium oxide and, possibly, some calcium residues included in the conglomerates of metallic thorium particles; in the electrolytic powder they were mainly thorium dioxide and the residues of electrolyte salts (fluorides and chlorides of thorium and the alkali metals). In addition, the powders obtained by both methods contained about 0.1% iron. Briquettes pressed out of these powders were of high porosity, and after sintering their density was not more than 10.5–10.7 gm/cm³. The sintered specimens were of low strength and of high brittleness.

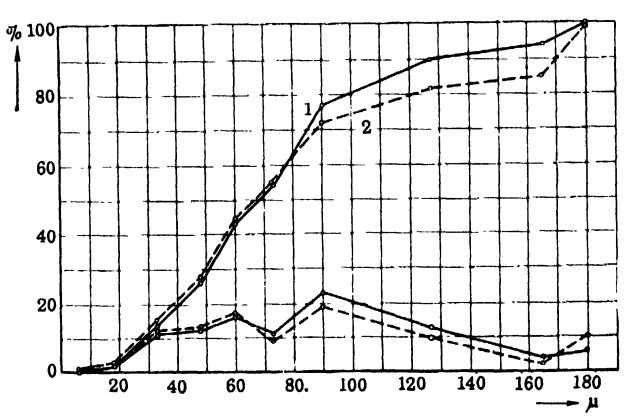

Figure 2. Particle size distribution of electrolytic (1) and calcium reduced (2) thorium powders

To reduce the impurity content in the powders, experiments were run on washing them with nitric acid subsequent to the water washing and table concentration.

Washing with acid of various concentrations was carried out in two stages:

Stage 1: 15% acid solution was used for the calcium reduced powder and 7% solution for the electrolytic one.

Stage 2: 2% nitric acid solution was employed to prevent hydrolysis of thorium nitrate formed during the first stage.

Washing with acid was followed by water treatment and subsequent drying with alcohol and ether. As a result of the acid washing, the thorium content was increased from 98.5–99% to 99.5–99.8%, the iron content decreasing to 0.02–0.04%. About 10% of the metal passed into the nitrate solution.

PROPERTIES OF THE ORIGINAL POWDERS

Typical chemical analyses of thorium powders obtained by various methods after washing with nitric acid are given in Table I.

The data in the table indicate that calcium reduced powder can be distinguished by an increased calcium content, and the electrolytic one by that of fluorine, owing to the use of thorium fluoride for electrolysis.

The average lattice constant for thorium powder is 5.070 kX, which corresponds to the theoretical specific gravity of 11.75 gm/cm³. The particles of the calcium reduced powder are sintered into polycrystalline conglomerates, dendritic in structure. The bulk density of the powder is 2.6–3 mg/cm³.

The particles of the electrolytic powder are spheroidal in shape with smooth surfaces; the bulk density of the powder being 4.5 gm/cm³. The electrolytic and the calcium reduced powders are similar to each other in particle size, their screen analysis averaging: +80 mesh, 6–11% by weight; −80 +250 mesh, 53–56% by weight; −250 mesh, 43–46% by weight.

Curves showing the particle size distribution of the electrolytic (1) and calcium reduced (2) thorium powders are represented in Fig. 2.

PRESSING

Effect of Compacting Pressure on Density of Briquettes Depending upon Thorium Powder Production Method

A study of the compressibility of thorium powders obtained by different methods showed that the calcium reduced thorium powder is of a lower compressibility than the electrolytic one.

Figure 3 shows that the curve of relative volume versus compacting pressure for a briquette of calcium reduced powder (2) lies above that for the

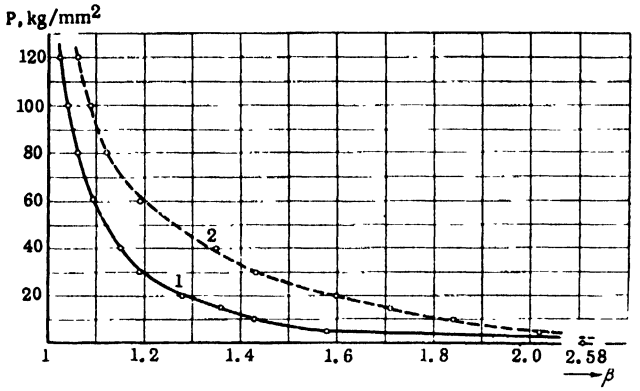

Figure 3. Influence of compacting pressure (P) on the changes in relative volume of pressed compacts (β) made of electrolytic (1) and calcium reduced (2) thorium powders

electrolytic one (1), i.e., it is shifted to the region of higher relative volumes. Thus, in order to obtain briquettes of equal density the pressure required for the calcium reduced powder is 1.5–2 times greater than for the electrolytic one.

From an examination of the pressing conditions of thorium powders the following conclusions may be drawn:

1. Thorium powder has a high plasticity and good compressibility.

2. The compressibility of thorium powder is affected by the method of production (the calcium reduced powder is harder than the electrolytic one), as well as by the degree of purity.

3. The pressure required to obtain briquettes with a density of 10.5–11.0 gm/cm³ and an $h:d$ ratio (h = height, d = diameter) of ~0.5 with pressure in one direction or ~1 with pressure in two directions, is 8–12 tons per cm² for the calcium reduced powder and 6–9 tons per cm² for the electrolytic one.

4. The high plasticity of thorium powder permits the use of high compacting pressures without causing slipping in the briquettes.

Sintering Process

The behaviour of the powders produced by the electrolytic and calcium reduction methods was compared in studying the conditions of thorium sintering.

The effects of the sintering temperature and the heating period on the density and tensile properties of the compacts were studied for both types of powders.

The briquettes were sintered in a vacuum furnace at a pressure of approximately 5×10^{-3} mm Hg.

ELECTROLYTIC METAL

Influence of the Sintering Temperature on the Mechanical Properties of Sintered Bodies

An investigation was carried out using compacts with an initial density of the order of 11 gm/cm³, at sintering temperatures ranging from 900 to 1500°C. The results obtained are shown in Fig. 4.

It follows from these data that the maximum value of strength (σ_b = 14–15 kg/mm²) is attained after sintering at 1100°C, and remains practically unchanged at the higher sintering temperatures.

Appreciable tensile elongation is observed beginning at a sintering temperature of 1000°C ($\delta \cong 10\%$). The elongation rises sharply with the temperature up to 1100°C ($\delta \cong 20\%$) and then continues to increase slowly up to the sintering temperature of 1500° ($\delta \cong 26\%$).

The high density obtained in the pressed compact does not change throughout the range of sintering temperatures studied.

The hardness of the sintered specimens (H_B of the order of 40 kg/mm²) also remains almost unchanged throughout this temperature range.

A study of the microstructure of the sintered compacts shows that recrystallization begins at a temperature of 1100°C. This promotes the formation of true metallic contact surfaces (boundaries between the newly formed grains), which is the reason for the sharp increase in strength and plasticity.

Thus, a temperature of 1100°C (about 0.7 melting point) may be suggested for sintering high-density compacts from the electrolytic powder. A more distinct polyhedric structure, resulting in somewhat higher strength and plasticity is observed at the sintering temperature of 1200–1300°C (~0.8 M. Pt.). However, as will be shown below cold pressing after sintering makes it possible to obtain a metal of high properties at a sintering temperature no higher than 1100°C.

Effect of Exposure on the Properties of Sintered Specimens at Given Sintering Temperature

This investigation was carried out using briquettes with an initial density of about 11 gm/cm³ at sintering temperatures of 1100 and 1300°C. The heating time was varied from 0.5 to 4 hours.

Figure 5 shows the influence of the sintering time on the properties of the specimens. The strength of the sintered specimens increases insignificantly from 13 to 15 kg/mm² with time at 1100 and 1300°C.

The influence of heating time (from 0.5 to 4 hours) on the plastic properties of thorium at a sintering temperature of 1100°C is characterized by an increase in its elongation from 15.3 to 21.6% and at 1300°C, from 22.5 to 29%. The figures characterizing the tensile properties of the sintered metal

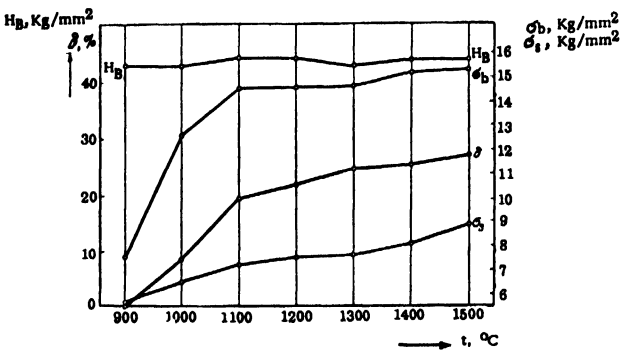

Figure 4. Influence of sintering temperature on mechanical properties of electrolytic thorium sintered specimens

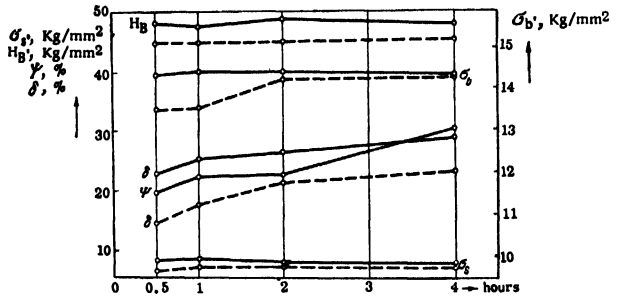

Figure 5. Influence of heating time at given sintering temperature on properties of electrolytic thorium sintered specimens. Uninterrupted line, 1300°C; interrupted line, 1100°C

indicate that at 1100° and especially at 1300° the sintering process and the formation of stable metallic contacts are completed on the whole in the course of half an hour.

CALCIUM-REDUCED METAL: EFFECT OF THE SINTERING TEMPERATURE ON THE MECHANICAL PROPERTIES OF SINTERED METAL

The study of sintering conditions for calcium-reduced thorium established that blisters and cracks appear on briquettes with densities greater than 10.3 gm/cm³ sintered at temperatures above 1150–1200°. This is due to the presence of residual metallic calcium oxide in the powder. On heating in vacuo, the oxide reacts with the metallic thorium to form metallic calcium. The latter has a comparatively high vapour pressure, and evaporates at the high sintering temperatures, causing failures in the continuity of the metal and forming blisters and cracks. This blistering on sintering was not observed in more porous briquettes having a residual porosity greater than 15% and with a predominance of pores passing right through the briquette. The calcium content in such sintered briquettes decreased from 0.1% in the initial powder to 0.05–0.03% in the sintered body.

In view of this, subsequent experiments on the study of the sintering process of calcium reduced metal were carried out using briquettes having an initial density of the order of 9 gm/cm³ (about 20% porosity). The average results of these experiments are shown in Fig. 6.

Unlike briquettes of the electrolytic powder with their high initial density which hardly changes on sintering, the porous briquettes of the calcium reduced powder are characterized by considerable shrinkage. Hence, changes in the tensile properties of the calcium reduced metal with sintering temperature depend to a great extent on the value of the residual porosity.

The hardness, strength and plasticity of the metal is increased with a rise in the sintering temperature and an increase in the density of the sintered bodies. The tensile strength is increased from 10 kg/mm² at 900°C to 22.5 kg/mm² at 1400°C, and hardness from 43 kg/mm to 75 kg/mm, respectively. The plastic properties of the specimens are low at all sintering temperatures, the elongation after sintering at 1400°C not exceeding 5%.

Thus, despite some residual porosity in the sintered calcium reduced metal, its strength and hardness are higher than those of the electrolytic one. At the same time the sintered calcium reduced metal is less ductile than the electrolytic one.

COLD PRESSING AND ANNEALING

To increase the density of the sintered bodies and to improve their tensile properties the possibility of compacts cold pressing with subsequent annealing was investigated.

The pressing was carried out in steel dies under a pressure of 10–14 tons per cm².

The pressed specimens were annealed for one hour under vacuum at a pressure of about 5×10^{-3} mm Hg and a temperature of 1100°C. The properties of the bodies after sintering, pressing and annealing are given in Table II.

This data indicate that pressing and annealing result in increasing the density, which is especially important for bodies made of the more porous sintered ingots of the calcium reduced metal, as well

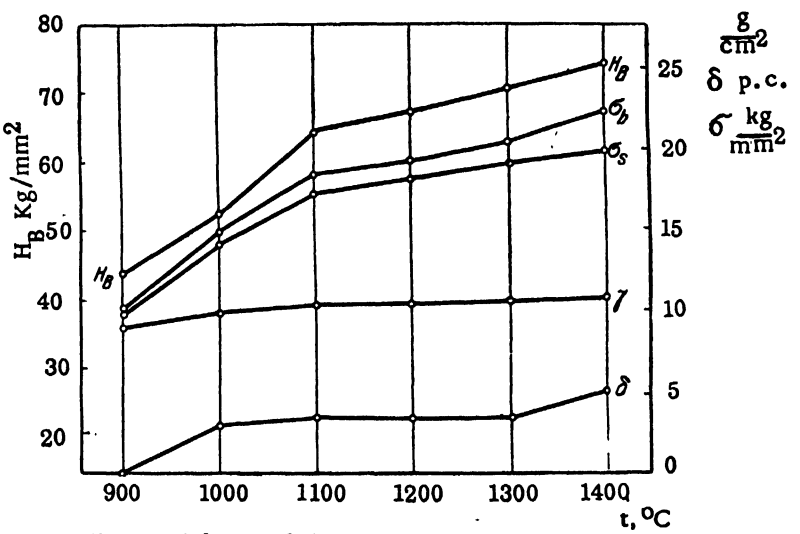

Figure 6. Influence of sintering temperature on mechanical properties of calcium-reduced thorium sintered specimens

Table II. Mechanical Properties of Sintered and Pressed Thorium Specimens

Original powder	*Sintering temperature °C*	*Characteristics of specimens*	*Density gm/cm³*	σ_b kg/mm²	σ_s kg/mm²	δ%	H_B kg/mm²
Electrolytic	1100	Sintered	11.30	14.7	7.8	28.0	50
Electrolytic	1300	Sintered	11.35	15.2	8.0	30.0	53
	1300	Pressed without annealing	11.60	14.6	13.8	0.0	84
	1100	Pressed and annealed	11.59	16.6	8.0	35.0	53
	1300	Pressed and annealed	11.62	16.6	8.3	43.0	51.3
Calcium reduced	1100	Sintered	10.77	17.6	11.0	10.3	69.0
	1100	Pressed and annealed	11.51	21.7	13.5	20.0	70.0
	1300	Pressed and annealed	11.55	22.1	13.7	17.4	70.0

as increasing tensile strength, hardness and plasticity.

A parallel increase in ductility, tensile strength and hardness accompanies changes in the technological conditions and is, in this case, specific for powder metallurgy products and does not coincide with the general principles regarding the changes in strength and ductility of cast non-porous metals.

Table III. Properties of Thorium Bodies Obtained by Powder Metallurgy Method from Calcium Reduced and Electrolytic Powders

Properties	*Electrolytic*	*Calcium-reduced*
Lattice constant, kX	5.07	
True, or X-ray density, gm/cm³	11.75	
Melting point, °C	1700 ± 20	
Density of compact metal, gm/cm³	11.60	11.50
Hardness, H_B, kg/mm²	52	70
Ultimate strength, σ_B kg/mm²	17	22
Yield strength σ_s kg/mm²	8	13
Elongation, δ%	35–43	17–23
Impact strength, a_k, kg-m/cm²	1.3	0.64
Linear thermal expansion coefficient 0–100 °C	$11.3–11.5 \times 10^{-6}$	
100–800 °C	$16.3–16.5 \times 10^{-6}$	
Specific resistivity, ohm.cm	$25–30 \times 10^{-6}$	
Thermal conductivity kcal/m-hr-°C	~ 37	

Besides improving the properties of the metal, the introduction of the compact pressing process after sintering makes it possible to lower the sintering temperature to 1100°C without deterioration of the properties of the metal.

Specimens of compact thorium obtained by the process described above were examined to ascertain physical and mechanical properties. The results are given in Table III.

Record of Proceedings of Session 15B.1

TUESDAY MORNING, 16 AUGUST 1955

Chairman: Mr. H. Brynielsson (Sweden)

Vice-Chairman: Mr. D. W. Seelman-Eggebert (Argentina)

Scientific Secretaries: Messrs. R. Hara and B. Prakash

PROGRAMME

P/407	Production of uranium metals	L. Grainger
P/341	The preparation of pure uranium metal	B. Goldschmidt and P. Vertes
P/636	Metallurgy of thorium	G. E. Kaplan
P/635	Powder metallurgy of thorium	G. A. Meyerson
	DISCUSSION	

Mr. P. V. DANCKWERTS (UK) presented paper P/407.

Mr. B. GOLDSCHMIDT (France) presented paper P/341.

Mr. G. A. MEYERSON (USSR) presented paper P/636 and P/635.

DISCUSSION OF P/407, P/341, P/636 AND P/635

Mr. A. WILHELM (USA): In connection with Mr. Grainger's paper, I have some comments to make with reference to the experience in the United States on the reduction of uranium tetrafluoride with Mg.

Magnesium reduction of uranium tetrafluoride was developed in the United States late in 1942 and was put into full scale production early in 1943. Yields of around 98 per cent of the metal can be readily maintained on a tonnage production scale by this process. The reaction between UF_4 and magnesium develops about 45 kcal less heat per mol of uranium than the well-known calcium reduction of the tetrafluoride. Therefore additional heat must be added to the UF_4 plus magnesium charge for the products of the reaction to reach a temperature sufficient to yield the metal and slag phases in the liquid condition and result in good separation.

This heat may be added by an auxiliary reaction, referred to as a thermal booster, or by pre-heating the charge to the ignition temperature. Either case can result in good separation of the phases. The latter, or pre-heating process, has been employed in tonnage production of uranium metal.

Since the temperature reached by the reacting charge in this reduction is well above the normal boiling point of magnesium, it is necessary to carry out the reaction in a closed vessel or bomb. The bomb is made of seamless steel pipe. In order to prevent reaction of the charge or products with the bomb, it is lined with a suitable refractory material such as "dead burnt" lime.

The lined, charged and closed bomb is set in a furnace maintained at around 600°C and allowed to heat until the reaction is initiated. After the reaction subsides the bomb is removed from the furnace and after cooling the massive piece of uranium, referred to as a "biscuit," is removed from the bomb. Charges yielding biscuits weighing about 40 lb each and 130 lb each were employed in the early production plant. A few special charges yielding 235 lb of metal in one piece were also employed. Further details of the process may be found in Paper P/817.

The CHAIRMAN: There is a question from Mr. F. H. Spedding (USA) to Mr. Meyerson on P/635:

"I should like to ask Mr. Meyerson what the oxygen content of the finished thorium product is, and how was this content determined?"

Mr. MEYERSON (USSR): The oxygen content in the powdered metal is evaluated from analysis figures for the total thorium content which I cited. The thorium content is 99.8%. The remainder is principally oxygen in the form of a thin oxide film surrounding each particle of the powder. Naturally, in the subsequent process of sintering in a vacuum this oxygen is not eliminated, since its chemical bond with the metal is very strong.

The CHAIRMAN: The next question is from Mr. F. G. Foote (USA), also to Mr. Meyerson regarding P/635:

"Have you melted any of your thorium? If so, how, and how did properties of the melted thorium compare with those of the sintered product?"

Mr. MEYERSON (USSR): We ran some tests on melting the thorium powder, both by heating it in beryllium oxide crucibles in the usual way and on the laboratory scale by heating it in an arc furnace in a water-cooled copper crucible. We found, however, particularly in the first case, that the quality of the thorium we melted in a fire-proof crucible was no better than that of the sintered product. On the other hand, the cast ingot always requires further processing—machining—which results in a considerable waste of metal. Consequently, since we did not

need to produce large ingots, we did not pursue the development of this method, but instead turned our attention to the powder metallurgy process which, as I showed, gives satisfactory results.

Mr. J. M. KAY (UK): I should like to put a question to Mr. Danckwerts. In his paper he mentioned the interesting possibility of using a fluidized bed technique for the dry stages of his process in going from uranyl nitrate to UF_4. Would he be willing to comment further on some of the chemical engineering problems in carrying out that process on an industrial scale?

Mr. DANCKWERKTS (UK): We have been doing some development work along these lines. Apart from the obvious attractions of a continuous process against a batch process such as I have described, the most startling result likely to come from the substitution of a fluidized bed reaction of the type used in the present "Dryway" plant rises from the fact that, of course, the mass transfer rates between the gas and the surface of the solid with which it is reacting will be very much higher in a fluidized bed than in the present "Dryway" type of reactor, in which the material is in a fairly thick layer on a tray and the gas merely blows over the top of the layer, so that all the action has to take place by diffusion of the gas into the layer. In the case of a fluidized bed, the solid is in the form of fairly small particles which are in rapid motion relative to the gas, and therefore the reaction is very much quicker. This, I think, may result in quite a startling reduction in the size of the plant required to produce a given quantity of the uranium.

We are actively engaged in pursuing fluidized bed techniques for the conversion of uranyl nitrate to uranium trioxide, and for the reduction of uranium trioxide to uranium dioxide, and for the transformation of this into uranium tetrafluoride.

Mr. J. MALY (Czechoslovakia): I have a question for Mr. Danckwerts. The precipitation of uranium peroxide from a weakly acid solution gives a purer product than the precipitation of ammonium uranate from an alkaline solution. Why is it that at the Springfield works uranium peroxide is precipitated before extraction and ammonium uranate after extraction? Why not the other way round?

I should also like to ask Mr. Danckwerts what materials were used in England for making the apparatus in which the various stages of the production of uranium metal were carried out after extraction of uranyl nitrate. In what atmosphere is the fusion of the uranium in the $UF_4 + Ca$ reaction carried out?

Mr. DANCKWERTS (UK): If I have understood it correctly, the first question is why we do not reverse the order of precipitation, precipitating with ammonia before peroxide. I take that to be the sense of the question, and I can only say that I do not know. This is now a matter of history. Presumably at the time that the factory was built this was the only process which had been worked out in the laboratory, and it was therefore incorporated in the factory. I am afraid that I have no other reason to give.

The second question, I think, refers to the fabrication of the uranium into fuel elements after the production of the metal billet. This is also done at the Springfields factory, but I did not include it in my talk today because I was not concerned with this kind of topic.

In mentioning the smelting of uranium I do not know whether the speaker refers to the reduction stage. If he does, I would say that the reduction stage, which is the reaction between calcium and uranium tetrafluoride, takes place at atmospheric pressure.

Session 15B.2

ANALYTICAL METHODS OF RAW MATERIAL PRODUCTION

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Analysis of Uranium and Thorium Raw Materials

By C. J. Rodden,* USA

The present article is a summary of the methods of analysis as applied to uranium and thorium ores and concentrates. In addition to methods for uranium and thorium, consideration is given to the determination of undesirable impurities in concentrates. It is realized that many other methods may be applicable but the ones given have proved satisfactory for the use intended.

SAMPLING

The problem of sampling uranium and thorium in ores and concentrates is a very important part of the over-all analytical program.

Owing to the high density of the mineral pitchblende and other uranium minerals, there is a tendency to segregate even under presumably normal sampling conditions. An example of this is given in the sampling of pitchblende ore. Originally a two-step Vezin sampler, Figs. 1 and 2, was used with a mixing barrel between the Vezins. Owing to dusting problems, this was changed to the arrangement shown in Fig. 3 where a mixing disc was used between the Vezins. With this arrangement it was found that segregation took place on the mixing disk due to differences in the density of pitchblende and the gangue material. Recent sampling has been done with a Galigher sampler which goes back and forth across the entire stream.

Concentrates of uranium in many instances contain a large proportion of UO_3. This compound has the characteristics of forming hydrates. The compound $UO_3 \cdot 2H_2O$ formed at low temperature will give up some of its water of crystallization, while UO_3 formed at a higher temperature will pick up water to form a hydrate. The extent of this hydration will be affected by the temperature and humidity. Materials of this type have been found very difficult to sample and then dry to a constant weight. A mixer-blender, Fig. 4, has been used with some success with this type of material. The material is not dried but is sampled on the "as received" basis. The blender is fitted with revolving choppers inside which break up clumps of material and give a uniform product. The choppers run at about 2000 revolutions per minute while the entire blender rotates at about 60 times per minute. The sample is then bottled, sealed and opened only when actually analyzed. The analysis is done on the "as received" basis with no further drying.

Thorium concentrates cannot be ignited without forming an oxide which is insoluble. When dried at lower temperatures, some concentrates have shown the same behavior as with uranium concentrates. In such instances the above mixer-blender has also been employed.

SEPARATIONS

Uranium

The methods for separating uranium from interfering elements are divided into two categories. In one, the uranium is separated from all other interfering elements, while in the other, the interfering elements are separated from the uranium.

In the first instance, solvent extraction is usually employed. This may be by the continuous diethyl ether extraction of a solution of the nitrate saturated with ammonium nitrate; [1,2] an ethyl acetate extraction of a nitrate solution saturated with magnesium or aluminum nitrate;[3,4] or a tributyl phosphate extraction of a nitrate solution.[5,6] These methods are used for residues and low grade ores, prior to a colorimetric or fluorimetric determination. In the extraction with tributyl phosphate a mixture of equal parts of tributyl phosphate and methyl isobutyl ketone or diethyl ether is used. There is better phase separation with this mixture than with tributyl phosphate alone. A nitrate solution containing 30% nitric acid by volume is extracted with the above mixture. After extraction, the organic layer is washed several times with a solution containing 5% potassium iodate in 30% nitric acid followed by a 30% nitric acid wash to remove any iodate. In this way any impurities, especially thorium and zirconium extracted by the tributyl phosphate, are removed. The uranium is stripped from the organic solution with a 25% ammonium acetate solution. The uranium can then be determined by any convenient method such as colorimetrically or fluorimetrically. The method is applicable to a variety of materials such as low grade ores and monazite sand.

The above method is not applicable in the presence of a large amount of thorium such as in the determination of uranium in thorium nitrate. In the case of thorium nitrate, the salt is heated to 400°C to 450°C to decompose the nitrate. The oxide is dissolved by heating in hydrochloric acid and a few milliliters of 5% hydrofluoric acid. The resulting solution is made up to contain 60 ml of hydrochloric acid per 100 ml of solution. This is extracted with tributyl phosphate-diethyl ether (1 to 1) and then the organic

* New Brunswick Laboratory.

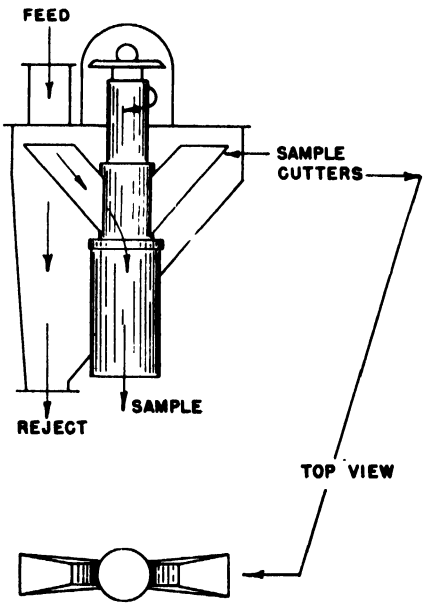

Figure 1. Simple Vezin sampler

phase is washed four times with 60%, by volume, hydrochloric acid. The organic phase is then washed once with 30%, by volume, nitric acid and then twice with a potassium iodate solution (5% in 30% nitric acid by volume). The remaining iodate in the organic phase is removed by washing once with 30%, by volume, nitric acid. The uranium is stripped from the organic phase with 25% ammonium acetate and determined either colorimetrically or fluorimetrically.

Occasional use is made of a cellulose column to separate uranium.[7] In this method ether is used to strip uranium from a nitrate solution which has been absorbed on a cellulose column.[8] The method is applicable to materials having a wide range of uranium concentrations.

The method generally used for the separation of impurities prior to the determination of uranium is that in which heavy metals are removed by a hydrogen sulfide precipitation followed by a cupferron-chloroform extraction in 10% sulfuric acid solution to remove insoluble cupferrates.[9] This procedure is used for high grade ores and concentrates.[10] In a variation of the above[11] the uranium is first precipitated as the phosphate which is then purified by a cupferron-chloroform extraction.

Thorium

The separation of thorium by solvent extraction using diethyl ether in 15%, by volume, nitric acid, after absorbing the solution of the nitrate on a cellulose column, has been used in some instances.[7] This procedure has the advantage that uranium and thorium can be separated from the same sample.

One of the most useful solvent extraction methods for separating thorium is that employing mesityl oxide to extract thorium nitrate from impurities.[12]

Of the precipitation methods, the one chiefly used in the analysis of high grade ores and concentrates is that employing a combination of the fluoride, hexamine and oxalate precipitation.[13]

GRAVIMETRIC METHODS

Uranium

The gravimetric determination of uranium is seldom employed at the present time, the disadvantage being that in most instances it is usually necessary to have a solution which contains uranium and no other impurities.

Precipitation with ammonium hydroxide followed by ignition, at 900°C under good oxidizing conditions, to U_3O_8 is occasionally employed. The ignition of uranyl nitrate after extraction with ether has been used. It has been found, however, that when uranyl nitrate is heated to the oxide, an excessively long time is required for complete conversion. If a small amount of hydrofluoric acid is added, the conversion time is shortened considerably.

Thorium

The gravimetric method for thorium is still the one most commonly used for the analysis of ores and concentrates. Thorium is usually separated from interfering elements by a potassium bifluoride fusion followed by a hexamine and oxalate precipitation.[13] The above procedure is used for contractual assay purposes. The precipitation as the peroxynitrate is employed for both high and low grade ores by the US Geological Survey.[14]

VOLUMETRIC METHODS

Uranium

In the volumetric determination of uranium the solution purified from interfering elements, generally by a cupferron extraction, is reduced in an

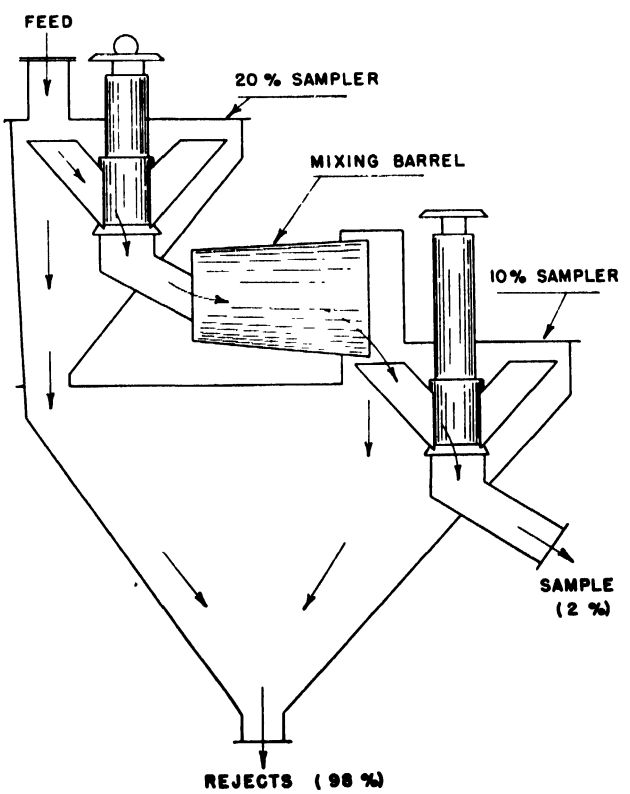

Figure 2. Twin Vezin with mixing barrel

amalgamated zinc reductor[15,16] to U^{4+} with some U^{3+}. The U^{3+} is converted to U^{4+} by aeration.[17,18]. The U^{4+} is oxidized to U^{6+} either by the use of potassium dichromate,[19,20] with sodium diphenylamine sulfonate as an indicator, or by ceric sulfate, with ferrous 1-10-phenanthroline sulfate as an indicator.[21] In the case of the dichromate titration, ferric chloride is used to oxidize the U^{4+} prior to titration. A precision of 1 part per thousand is usually obtained with both methods. Occasional use is made of the permanganate titration method.[18] The use of an added indicator,[22] ferrous 1-10-phenanthroline, is helpful with the permanganate titration.

Thorium

Volumetric methods for thorium are rarely employed except on essentially pure materials such as thorium nitrate where the disodium salt of ethylene diaminetetra-acetic acid is used with Alizarin Red S as the indicator.[23,24]

This method has been used after separation of thorium from interfering elements with a mesityl oxide extraction of the nitrate.[25]

COLORIMETRIC METHODS

Uranium

While some reagents are more specific for uranium than others, in general, a separation prior to a colorimetric determination is necessary. The alkaline peroxide method[2,26] is widely used for low grade concentrates and plant products. It is generally used after separating the uranium by an ether extraction. The thiocyanate method[27,28] is used to a considerable extent in the analysis of low grade ores. It is used, after separating the uranium by an ethyl acetate extraction, either directly in the acetate solution[29] or after stripping the acetate solution with water.[28] The oxine procedure[6] has proved quite successful for the analysis of various mineral concentrates. It has the advantage of stability of color and sensitivity to low concentrations of uranium. It has the disadvantage that essentially all impurities must be removed. This is readily done by a tributyl phosphate separation in strong nitric acid and back washing the solvent layer with nitric acid to remove impurities.

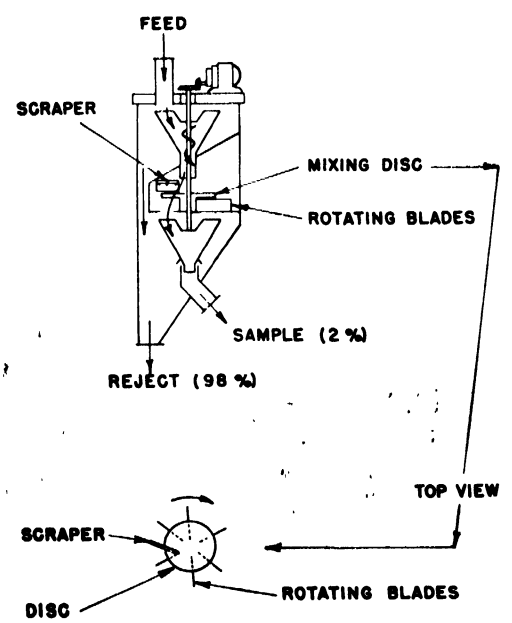

Figure 3. Twin Vezin with mixing disc

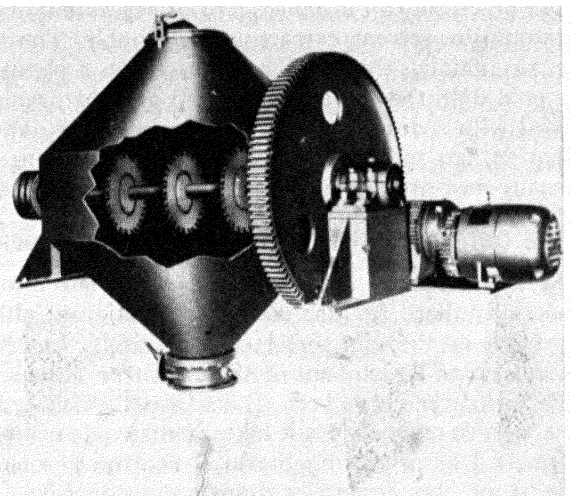

Figure 4. Mixer-blender

Thorium

The method most commonly used is based on the red color developed with 1-(*o*-arsenophenylazo)-2-naphthol-3-6 disulfonic acid.[30,31,25] The method is useful for the determination of thorium in low grade ores and tailings. It has been applied to monazite[25] after separation of the thorium with mesityl oxide and to uranium concentrates after separation with tributyl phosphate.[5]

POLAROGRAPHIC METHODS

The polarographic method is occasionally used for the determination of uranium in ores and concentrates. Tributyl phosphate may be used to extract uranium from impurities.[32] A polarographic wave is given by uranium when the tributyl phosphate is diluted with glacial acetic acid, and ammonium acetate is added as the electrolyte. The wave has a half-wave potential of about −0.7 volts versus the mercury pool electrode, and the wave-height is proportional to the uranium concentration.

For the determination of uranium the tributyl phosphate extract is diluted with at least four parts of glacial acetic acid containing 2%, by volume, of water. A suitable concentration of ammonium acetate is 0.25*M*. The method is satisfactory for the determination of uranium in concentrations down to 20 γ of uranium per milliliter of tributyl phosphate.

FLUORIMETRIC METHODS

The fluorimetric method is used for the analysis of low grade ores and tailings. It is also used for the determination of uranium in thorium ores and concentrates.

In practically all instances a prior separation of the uranium by solvent extraction is desirable. The solvent containing the uranium is placed on a platinum or gold disc, the solvent volatilized and the uranium fused with sodium fluoride[33] or a mixture of sodium fluoride and sodium carbonate.[4] The fluorescence is usually measured in a reflection type of fluorimeter.[34]

THE DETERMINATION OF NEUTRON ABSORBERS

The presence of neutron absorbers in concentrates especially those for use in the preparation of either uranium or thorium metal is undesirable. In order to determine the amount of these neutron absorbers, two approaches have been made. One, the "shotgun" analysis, so named since it takes in many elements, is a method of measuring the total neutron absorbing effects of the impurities present in uranium and thorium materials in terms of boron. The other approach is to determine each of the individual elements and determine the absorption effects by calculation from the individual capture cross section of the elements.

"Shotgun" Method

The method employed for the "shotgun" procedure[35,36] is to extract the uranium or thorium from the impurities by solvent extraction. In the case of uranium the sample is converted to the nitrate and extracted with diethyl ether. After washing the ether extract and combining the washings with the aqueous, layer, the combined aqueous layers are boiled down and another ether extraction is made on the aqueous layer. This process is repeated until the final amount of uranium oxide left containing most of the neutron absorbing impurities present in the original sample is reduced to 2 to 8 grams. In the case of thorium, a tributyl phosphate extraction is done in the same manner as uranium.

An arrangement for making accurate neutron absorption measurements requires a high neutron flux, properly collimated and thermalized. Paraffin has been employed as a moderator to obtain adequate thermalization of the fast neutron flux. The neutron intensity is measured by a boron film counter, which is dependent on the $B^{10}(n,\alpha)Li^7$ reaction.

A convenient source of neutrons to use for the neutron absorption apparatus is a radium-beryllium mixture. The neutron energies from this source, however, are high and range from 2 to 13 Mev.[37] The neutrons must be passed through a moderator to slow them to thermal energies.

A hydrogenous moderator has the duel advantage of a high scatter and a small capture cross section. Further, the smaller the mass of the nucleus with which the neutron collides, the more energy it gives up. The fraction of the slow neutron beam absorbed on passing through the sample can be calculated to a first approximation by the equation,

$$I/I_0 = e^{-N\sigma x}$$

where I and I_0 are the final and initial intensities of the incident particles expressed as number of particles /cm^2-sec; N is the number of atoms per cubic centimeter of target material; σ is the cross section of target material expressed as square centimeters of effective area per nucleus; and x is the target thickness in centimeters.

The neutron source is a radium-beryllium mixture (2.5 gm Ra + 7.5 gm Be) enclosed in a Monel metal capsule. The moderator used to thermalize the fast neutrons of the source consists of paraffin.

The apparatus[38] used is shown in Fig. 5.

The counter is a disc-type proportional methane flow counter. The counting volume is defined by two parallel plates, one of which is coated with enriched B^{10} and a rectangular support for the central high voltage wire network. The care taken in construction, and handling of the counter is critical. The details of construction of the counter are shown in Figs. 6 and 7.

The boron coated aluminum disc is approximately one inch in diameter, and has a coating of 4.4 mg of enriched B^{10} plated evenly over it. The collecting electrode used is a tungsten wire 0.002 inch in diameter. The tensile strength of tungsten is high and the wire used was relatively free of irregularities as determined by microscopic inspection. The holes in the inside aluminum rectangle are drilled accurately and the wires kept under tension so that a uniform electric field can be obtained in the counter. Tension on the wires is maintained by placing a small coil of spring wire under the glass U-shaped insulators as shown in Fig. 7. One end of the wire is anchored in a glass bead formed in the end of a short length of glass tubing and the other brought out to the high voltage connector through a glass tube.

The distance between the wires and the distance between the two parallel plates is such that the most

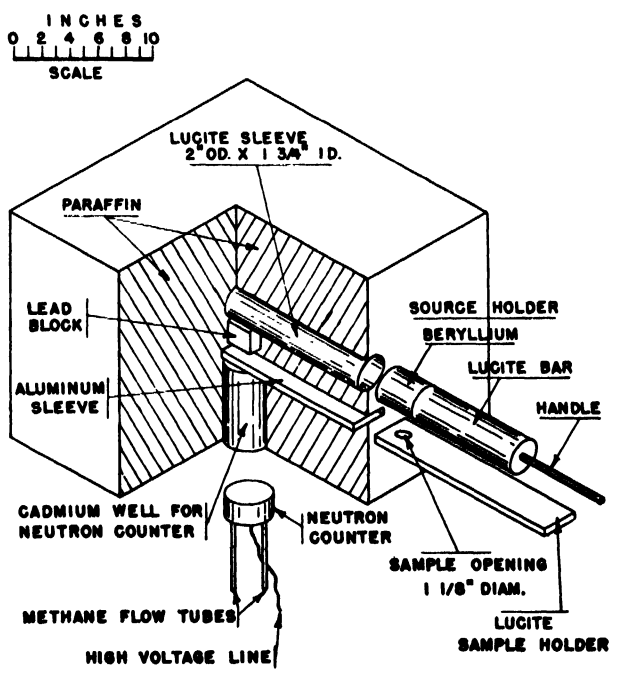

Figure 5. Neutron absorption apparatus

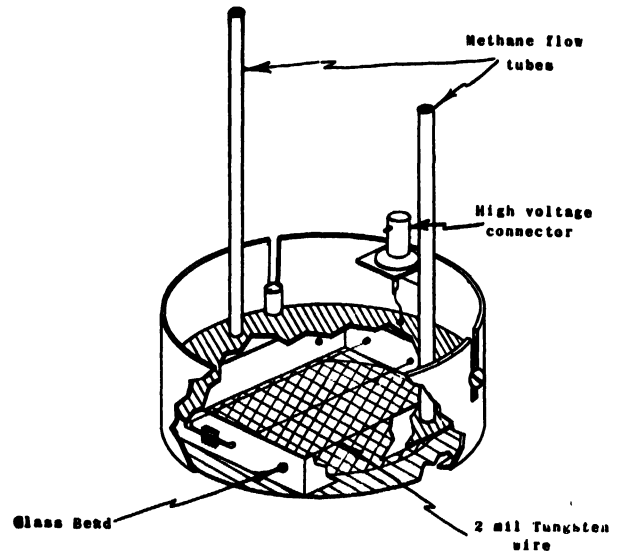

Figure 6. Neutron counter

energetic alpha particle can expend all its energy in the gaseous volume of the counter. The range of the alpha particle from the $B^{10}(n,\alpha)Li^7$ reaction is 0.7 cm,[39] and this value was used in spacing components.

Methane flows in and out of the chamber through two aluminum tubes mounted in the top plate. The flow pattern was quite effective since the counting rate reached a maximum within minutes after turning on the methane flow. Mounted on the top plate also was a high voltage connector for connection to the scaler.

The counting apparatus used had a plateau with a slope of 17% per 100 volts at 2400 volts.

Uranium source materials used in neutron absorption measurements are made into 8 gram pellets,[36] which are about $\frac{3}{16}$ inch in height and 1 inch in diameter, at a pressure of 10 tons per square inch. The material used to make the pellets was first finely pulverized with a mortar and pestle, then carefully weighed out and transferred to a die. If insufficient oxide was obtained from the extraction, additional pure uranium dioxide is added to give an 8-gram pellet.

Standards are prepared by mixing 8 grams of uranium dioxide with 0.5 to 15 mg of boron as boric acid.

The optimum source to counter distance is determined by measuring the neutron flux, C_{Cd}, transmitted by a sheet of cadmium 0.25-mm thick, and the unattenuated flux C_0, for which the ratio $C_{Cd}/(C_0 - C_{Cd})$ is a minimum (about 13 cm).

The per cent absorption of slow neutrons by the impurities in a sample is given by

$$\% A = \frac{(C_0 - C_{Cd}) - (C_x - C_{Cd}) - (C_0 - C_u)}{C_0 - C_{Cd}} \times (100)$$

$$\% A = \frac{C_u - C_x}{C_0 - C_{Cd}} \times 100$$

where A is the fraction of slow neutrons absorbed by the impurities in the sample, C_0 is the counting rate of the unattenuated neutron beam, C_{Cd} is the counting rate of the neutron beam after absorption by a 0.25-mm thick sheet of Cd, C_u is the counting rate of the neutron beam after absorption by pure uranium equivalent to that contained in the sample, and C_x is the counting rate of the neutron beam after absorption by the sample.

Chemical and Spectographic Methods

Carrier Distillation Method

The most satisfactory method for detecting most elements is the spectrochemical method employing the carrier distillation technique. The methods have changed but slightly since originally published.[40,41] The method is also directly applicable to thorium oxide. A list of the elements determined by this method is given in Table I.

Unfortunately, this method does not apply to the rare earth elements, the refractory group elements of zirconium, hafnium, niobium and tantalum; and to the platinum group elements. A concentration prior to spectrographic analysis is necessary with these elements. The refractory group elements are separated by extracting a sulfate solution of the elements containing 10% sulfuric acid with cupferron and chloroform. Bismuth is usually added as a spectrographic matrix and carrier before extraction. The cupferron-chloroform solution is then evaporated and cautiously ignited to the oxide. The platinum group is generally collected with gold as a carrier.[42]

Separation of Rare Earths from UO_3

The separation of the rare earths from uranium trioxide[43] is carried out by (1) extraction of the uranium from a hydrochloric acid solution with tributyl phosphate, (2) isolation of the rare earths by successive precipitation with sodium hydroxide and ammonium hydroxide in the presence of hy-

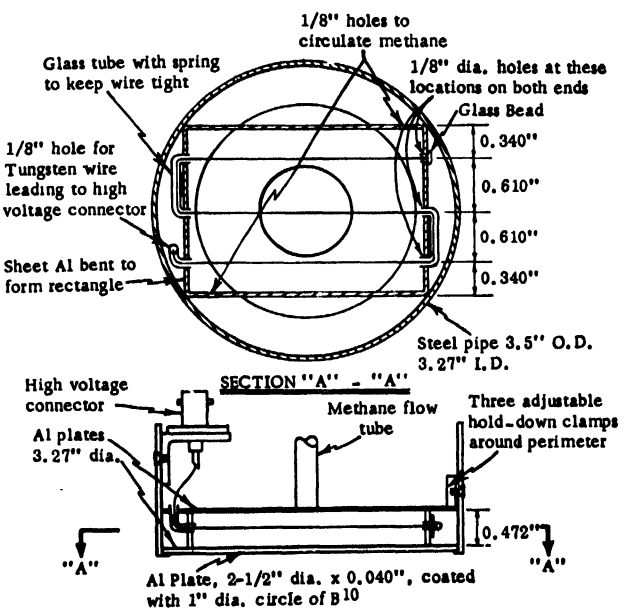
1/8" holes to circulate methane
Glass tube with spring to keep wire tight
1/8" dia. holes at these locations on both ends
Glass Bead
1/8" hole for Tungsten wire leading to high voltage connector
0.340"
0.610"
0.610"
0.340"
Sheet Al bent to form rectangle
Steel pipe 3.5" O.D. 3.27" I.D.
High voltage connector
SECTION "A" - "A"
Methane flow tube
Three adjustable hold-down clamps around perimeter
Al plates 3.27" dia.
0.472"
"A"
"A"
Al Plate, 2-1/2" dia. x 0.040", coated with 1" dia. circle of B10

Figure 7. Detail of neutron counter

Table I. Elements Determined by Carrier Distillation Method

Element	*Sensitivity, ppm*	*Element*	*Sensitivity, ppm*
Ag	0.05	Mg	0.5
Al	5	Mn	1
As	5	Mo	1
Au	0.3	Na	150
B	0.08	Ni	2
Be	0.1	P	50
Bi	0.5	Pb	1
Co	1	Sb	10
Cr	3	Si	3
Cu	0.3	Sn	1
Fe	1	Tl	3
Ge	0.2	V	5
In	0.5	Zn	20

drogen peroxide and (3) ignition of the rare earth hydroxides to oxides.

Dissolve 10 gm uranium trioxide in 50 ml of 6*N* hydrochloric acid and transfer the solution to a 250 ml separatory funnel. Wash the beaker with 25 ml of 6*N* hydrochloric acid and add the washing to the same funnel. Remove the uranium by repeated extractions with 100 ml portions of tributyl phosphate. (In general, three such extractions are sufficient to remove the uranium.) Remove residual tributyl phosphate from the aqueous phase by extracting with 50 ml of equal parts "Solvesso" (kerosene) and diethyl ether.

Add 1.0 mg of lanthanum (chloride solution) and 1 ml of 30% hydrogen peroxide to the aqueous solution. Precipitate the hydroxides by adding a freshly prepared strong sodium hydroxide solution until the solution is just alkaline and then add a few milliliters in excess. Digest on a steam bath for ½ hour. Add one-half of a macerated Whatman Accelerator (1 × ¾ inches). Filter through Whatman No. 42 paper with the aid of a Fisher Filtrator. Wash precipitate and paper with concentrated ammonium hydroxide.

Dissolve the precipitate from the filter paper with 50 ml of hot 1 : 2 hydrochloric acid. Add 1 ml of 30% hydrogen peroxide and reprecipitate the hydroxides with ammonium hydroxide by first neutralizing and then adding 10%, by volume, in excess. The hydroxides are filtered and washed as above and then ignited to the oxides in a tared platinum crucible. The rare earth concentrate is weighed and then analyzed spectrochemically for the individual rare earths.

Separation of the Rare Earths from Thorium Nitrate

The separation of the rare earths from thorium nitrate[82] is carried out by (1) extraction of the bulk of the thorium with dibutoxytetraglycol-diethyl ether mixture; (2) extraction of the residual thorium and other impurities such as iron with 8-quinolinol in chloroform; (3) precipitation of the rare earths with ammonium hydroxide and ignition to the oxides.

Equilibrate 280 ml of dibutoxytetraglycol (pentaether) and 140 ml of diethyl ether with 250 ml of 8*M* nitric acid in a 2 liter separatory funnel and discard the aqueous phase.

Add 50 gm of thorium nitrate tetrahydrate and 7.0 ml of concentrated nitric acid to 300 ml of the pentaether-diethyl ether mixture in a 500 ml separatory funnel and shake until the salt is dissolved. Drain the aqueous phase into a 250 ml separatory funnel. Wash the organic phase with 15 ml of 8*M* nitric acid and combine the aqueous phases. Discard the organic phase, extract the combined aqueous phase with 200 ml of pentaether-diethyl ether mixture. Drain the aqueous phase into a 150 ml beaker. Wash the organic phase with 10 ml of 8*M* nitric acid and combine the aqueous phases. Discard the organic phase.

Dilute the solution to about 100 ml. Add 10 ml of glacial acetic acid and adjust the pH to about 2.0 with concentrated ammonium hydroxide. Cool the solution in an ice-bath, add 3.0 gm of 8-quinolinol and adjust the pH to 4.2 with concentrated ammonium hydroxide. Transfer the contents of the beaker to a 250 ml separatory funnel. Extract with five 10 ml portions of 8-quinolinol in chloroform (12 gm/50 ml) and wash with 25 ml portions of chloroform.

Transfer the solution to a 250 ml beaker. Add 1.0 mg of lanthanum carrier as a solution of the nitrate and 50 mg of titanium as a solution of the sulfate to serve as a spectrographic internal standard. Add about 10%, by volume, of concentrated ammonium hydroxide and heat until the precipitate flocculates. Filter the hot solution through Whatman No. 42 paper and ignite the precipitate to the oxides in platinum. The rare earth concentrate is weighed and then analyzed spectrochemically for the individual rare earths.

Boron

The above spectrographic methods are dependent upon having proper standards and this is relatively simple except in the case of boron where some of the boron may be lost in the chemical operations.

In the case of uranium, the standard uranium oxide samples are analyzed by the following procedure which may also be used for other uranium and thorium compounds. Thorium oxide samples, once they have been highly ignited, are very difficult to to dissolve and it is generally preferable to analyze a low-fired (less than 400°C) oxide sample for boron before final ignition.

Colorimetric Determination of Microgram Amounts of Boron[44]

Quantitative colorimetric methods for the determination of boron in very small amounts in solution were first suggested by Robinson[45] and Naftel,[46] both of whom developed procedures based on Cassal and Gerrans' method[47] in which an alkaline borate solution is evaporated to dryness, treated with oxalic acid, hydrochloric acid and turmeric, and then dried under controlled conditions. The red color formed in the presence of boron is then dissolved in alcohol and compared with that of similar solutions containing known amounts of boron. The procedures differ in

respect to the kind of alkali used, method of obtaining intimate mixture of reacting substances at the drying point, means of adding turmeric, drying conditions, and facilities for comparing color. Rodden and Scherrer[44] found Naftel's procedure satisfactory for the routine analysis of test solutions containing 0.1 to 1.5 γ boron and applied the procedure to uranium compounds.

The colorimetric procedure is suitable for the estimation of 0.1 to 1.5 γ of boron with a precision of ± 10 per cent. However, the over-all accuracy depends on the completeness of the boron separation and the size aliquot taken for color development. The maximum amount of sample taken for distillation is limited by its type and solubility, i.e., about 2 gm of U_3O_8.

Phosphoric acid solutions of uranium form gels when diluted with methanol. In the National Bureau of Standards (NBS) distillation procedure, this is avoided by distilling methanol through the hot sample solution and thus limiting the dilution.

Separation of Boron by Distillation from Phosphoric Acid (NBS)

The distilling apparatus, shown in Fig. 8, is similar to that described by Robinson.[45] It consists of two 50 ml quartz Kjeldahl flasks (*A* and *B*), quartz tubing (4 mm id), rubber stoppers, a glass condenser, and a boron-free glass receiving flask (*C*). The alcohol flask, *B*, is provided with a boiling tube and a safety tube, all of quartz.

Analytical reagent phosphoric acid, 85%, containing less than 0.05 γ boron per milliliter is used without purification. If the boron content is too high it may be lowered by repeated circulation of methanol vapors, distilled from sodium hydroxide, through the phosphoric acid which is heated by a water bath. The methyl phosphate formed may be hydrolyzed by the addition of water and then the alcohol and water may be both removed by further distillation.

Purified methanol is prepared by distilling reagent absolute methanol from potassium or sodium hydroxide in a quartz apparatus.

Calcium hydroxide suspension (0.1*N*) is prepared from calcium hydride or from the hydroxide or oxide which is prepared from distilled calcium containing 0.1 ppm or less boron.

Sodium carbonate containing 0.1 ppm or less boron is prepared by dissolving analytical reagent, boron-free sodium in purified methanol in a quartz dish, diluting with water, saturating with tank carbon dioxide, drying and baking on a hot plate.

Procedure for U_3O_8

Five milliliters of the lime suspension is placed in the receiving flask, *C*; 25 ml of the purified methanol and a pellet of sodium hydroxide in flask *B;* and the sample and 10 ml of phosphoric acid in flask *A*. After gently but firmly connecting all flasks to the still, *A* is heated with a tiny flame until the sample is in solution. The flame is removed, and while the solution is still hot, a 400-ml beaker of hot water is placed so as to envelop flask *B* and heated to 75 to 85° until about three-fourths of the alcohol has distilled over. The flame is extinguished and 25 ml of purified methanol is added through the safety tube. As soon as alcohol starts passing through flask *A*, it is surrounded with a 400-ml beaker of hot water and heated to boiling until no more alcohol distills or until the quartz tube leading to the condenser is cold. Flask *B* is heated again as above. The distillation is continued until from 50 to 100 ml of alcohol, depending on the type of sample, has been distilled from flask *B*. Water bath, *A*, is filled each time alcohol starts passing through the sample, and heated until no more alcohol distills off. At the end of the distillation, the burners are extinguished, the flasks loosened from the stoppers, and the end of the condenser tube washed with water. The contents of the receiver are acidified with hydrochloric acid (usually 2 drops) and reserved for the determination of boron, being diluted to 100 ml, or other convenient volume just before use. A blank determination is made on the phosphoric acid.

Determination of Boron in Distillate[46]

Porcelain evaporating dishes are satisfactory if they are the same size and are well glazed. Three inch dishes are convenient for 20-ml samples.

Turmeric extract is prepared by stirring 1 gm of turmeric in 100 ml of 95% ethanol for 2 to 3 hours, and filtering. Boron-free containers are used and the extract is stored in the dark.

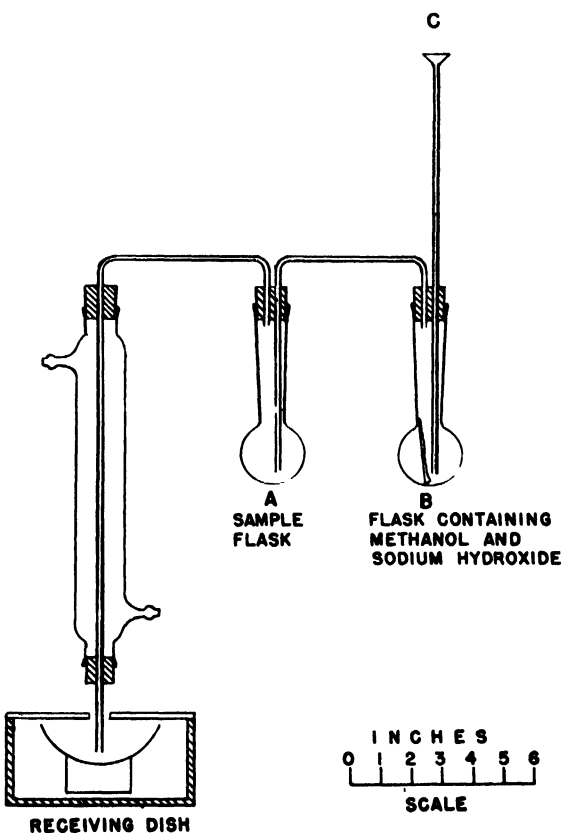

Figure 8. Distillation apparatus

A stock oxalic acid solution (20%) is prepared by dissolving 80 gm of $(COOH)_2 \cdot 2H_2O$ in 350 ml of water, and is stored in quartz. The oxalic-hydrochloric mixture is prepared just before using by warming the 20% (wt/vol) oxalic acid solution to 60°C to dissolve all crystals, and then mixing 4 vols of the solution with 1 vol of concentrated hydrochloric acid.[22]

The sample distillate or extract, or preferably an aliquot which contains about 0.5 to 1.0 γ of boron, and not more than half a drop of concentrated hydrochloric acid, is mixed with the lime suspension in a porcelain evaporating dish; there should be a 5 ml excess of 0.1*N* lime. The mixture is evaporated to complete dryness on a steam bath and then cooled to room temperature. One milliliter of the oxalic-acid-hydrochloric-acid solution is added and the dish is manipulated so as to bring the acid reagent in contact with all the residue. Then 2 ml of the turmeric extract is added and the dish is swirled to mix the contents thoroughly. The dish is floated in a water bath, kept at 55°C ± 1°C, and allowed to remain until 30 minutes after the contents are dry. The dish is cooled to room temperature and the residue is extracted with 95% ethanol. The mixture is stirred with a rubber policeman and then quantitatively centrifuged or filtered. The clear liquid is diluted to volume (15 to 25 ml) with ethanol and mixed. The transmittance of the solution at 540 mμ is measured spectrophotometrically against a reference solution obtained by carrying a cacium hydroxide blank through the color development. The boron content of the test solution is found from a transmittancy-concentration curve prepared by direct color development of known amounts of boric acid (0.5 to 1.5 γ). Since this curve shifts from day to day, at least two standards should be developed with each set of samples.[48] After correcting the amount of boron in the test solution for the distillation or extracting blank, the boron content of the sample is calculated.

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Physico-Chemical Methods of Uranium Production Control

By A. P. Vinogradov, USSR

Thanks to known theoretical researches we have been able within a short period of time, to work out a series of physical and physico-chemical methods of quantitative determination of uranium and of impurities in pure uranium, particularly in the optical and X-ray spectra field, in electro-chemistry and in other fields.

Since there is only a small quantity of impurities, these methods possess adequate precision, considerable sensitivity and good reproducibility. Their main advantage, as compared to many chemical methods, is their capacity for extremely rapid analysis.

There are essentially two analytical problems that have arisen since the beginning of uranium production—control of the technological process and control of uranium with respect to impurities.

For this purpose numerous chemical methods of analysis have been worked out, as well as methods based on uranium radioactivity, on luminescence, etc. Experiments in spectral and X-ray spectrographic analysis, polarography and other physico-chemical methods, carried out jointly with chemical methods, have yielded quite satisfactory results. A possibility, however, arose to utilize these physical and physico-chemical methods for direct determination of uranium or its impurities without any preliminary chemical preparation. This was achieved and, thanks to the rapidity and reliability in determination, such methods have become an important factor in the control of uranium production. This paper throws light on the researches concerned with the development of direct physico-chemical methods of determining uranium and its mixtures on a large scale, without preliminary chemical separation or concentration.

We shall deal only with certain methods of spectral determination of impurities in pure uranium, its oxide, etc.; of spectral determination of uranium itself in ores, particularly with making use of isotopes U^{235} and U^{238}, of X-ray spectrographic determination of uranium in minerals and especially of the determination by this way, of rare earths in uranium, then of polarography and oscillographic polarography of uranium and its impurities.

Original language: Russian.

QUANTITATIVE SPECTRAL DETERMINATION OF IMPURITIES IN URANIUM

To determine impurities in pure uranium or in its oxide, particularly neutron-active impurities, namely Li, B, Be, Cd and others, the method must possess sensitivity of at least $10^{-5}\%$ and adequately good precision. Although the spectral method at $10^{-5}\%$ made possible the quantitative determination of only alkaline elements, it suggested the possibility of using this method in the analysis of impurities in pure uranium as well.

Systematic researches showed, however, that one could not expect success simply by selecting excitation methods by working in the atmosphere of inactive gases, etc. We had to look for new ways. The difficulty of the task of determining the impurities in uranium was complicated by the fact that the uranium spectrum consists of a large number of relatively weak lines, situated on an extremely intense background.

It was essential to find ways for radically decreasing the number of lines in the uranium spectrum and for eliminating or weakening the continuous uranium spectrum. It was necessary to obtain pure electrodes whose impurities would not interfere with quantitative determination.

The simplest solution of the problem of determining the impurities in uranium was the method of evaporating the impurities (Mandelshtam, Turovtseva and Semyonov), which makes use of the differences in volatility of uranium oxide and of its impurities.

It was proposed to divide simultaneously the process of impurity evaporation from the process of spectrum excitation of impurities transmitted to the electrode.

Evaporation led to practically complete separation of most of the impurities from the bulk of the uranium. At the same time the process of relative concentration on the electrode was taking place. At first we made use of various carriers. Then it became possible to evaporate the impurities without any carriers.

Determinations were carried out as follows: in the first instance pure uranium was ignited and converted to U_3O_8, then the oxide($\sim$ 100 mg) was placed in a graphite crucible. After this, the crucible was heated by passing a current through it up to

1800–2000°. Under these conditions, as numerous investigations have shown, a considerable part of the impurities, including the nonvolatile Zr, Ti, Th and others, evaporated within 1 minute (Fig. 1).

The vapours of these impurities were condensed either on a graphite or on a water-cooled metal electrode. Subsequently, these electrodes were used either as arc anodes, or as spark electrodes. The absence of losses, i.e., the full evaporation of the impurities, was checked by spectroscopic methods and, as shown later, also by radioactive indicators.

Evaporation could be regulated by selecting the temperature of heating the graphite crucible. For this purpose a special evaporator was constructed.

Owing to the processes of separation and spectrum excitation, it was easy to select the most favourable source of excitation and the optimum conditions suitable for the nature of impurities determined.

Owing to condensation of impurities on the electrode surface (for instance, graphite) high purity of the electrode material was not sought. This is a very important factor, since the production, for instance, of graphite electrodes free of boron ($< 10^{-6}\%$) presented an extremely complicated problem. Although complete evaporation of the mixtures was not essential since the sample and the standard underwent the same operation, it was checked, as already mentioned, by radioactive indicators.

Various radioactive elements, one isotope or several radioisotopes, were introduced into pure oxide U_3O_8 (specially purified to be used with etalons). Their quantity was determined in the usual way, by γ- or β-counting. After evaporation, γ- or β-activity

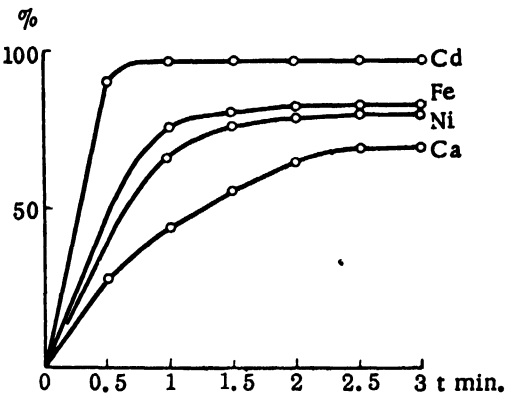

Figure 1. Dependence of complete evaporation of elements on time at a temperature of 1800°C

was determined in the U_3O_8 which was left in the graphite crucible as well as on the electrodes. We noted the diffusion of the radioisotope into the graphite crucible wall. This activity was likewise measured and a corresponding correction was made in counting. The results of the radiometric and spectral determination coincided well.

Table I gives some data on the complete evaporation obtained by the radioactive method (Beliaev).

This and other data show that at $t° = 1800°$–$2000°$, a considerable quantity of impurities evaporate, 81–98%.

For the construction of a working curve we used etalons.

The spectra of the sample and etalons were obtained on an ISP-22 spectrograph. Concentration of impurities was determined using a working curve of S versus log C (see Fig. 2). From the internal

Table I. Complete Evaporation (in %) of Impurities in U_3O_8, at 760 mm in the Air. Time of Sublimation — 2 minutes; Weighed Sample — 30 mg

t°C / *Elements and indicators*	1000	1200	1400	1600	1800	2000
Cd^{115}†	92	94	96	98	98	91*
Sb^{112}	90	96	98	98	97	96*
Bi^{210}	89	91	93	94	96	94*
Pb^{209}	79	82	90	92	94	95
Sn^{121}	52	70	72	82	85	91
Mn^{56}	48	52	64	78	82	86
Cu^{64}	41	56	72	81	83	85
Fe^{59}	6	9	25	62	72	84
Co^{60}	8	12	31	65	78	87
K^{42}	20	43	61	72	87	88
Na^{24}	15	38	63	74	87	89

* Decrease of complete condensation of Cd, Sb, Bi at 2000°C is caused by the reverse evaporation from the condensing capsule, as a result of a strong heating of the latter.

† The isotope which was used in research.

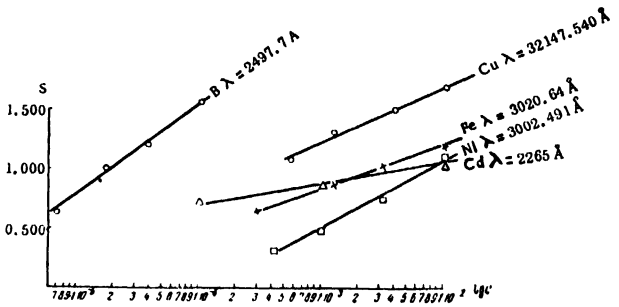

Figure 2. Working curve for the determination of B, Cu, Fe, Ni and Cd in uranium

standard and using $\Delta S - \log C$, the sensitivity of the method was 10^{-4}–10^{-5}%. In many cases it could be increased by selecting optimum conditions for any specific impurities.

Table II contains data on the sensitivity of the method (in weight %) as compared to the sensitivity of Scribner and Mullin's method.[1] As is known, it is based on the excitation of directly evaporating impurities, without preliminary condensation.

As the table shows, the method of evaporation has a considerably higher sensitivity for all elements than Scribner and Mullin's method.

The reproducibility of the method was checked by repeated analyses of impurities in the same sample. As an example Table III gives data which show the reproducibility of boron determination in uranium obtained by normal manufacture. The average arithmetical error in the determination of boron and other impurities (without internal standard) is between 10% and 15%.

The time required for determination of impurities is about 2 hours.

The method of evaporation, possessing a number of advantages over other usual spectral methods, is certainly applicable to many other substances.

SPECTRAL DETERMINATION OF SMALL AMOUNTS OF URANIUM IN ROCKS, ORES AND INTERMEDIATE PRODUCTS

Spectral quantitative determination of small uranium amounts in rocks, ores and other materials is a difficult task. This, in particular, explains the almost complete lack of such investigations and practical results.[2,3,4]

In the Soviet Union this work was started by V. K. Prokofiev, but the methods he proposed required preliminary chemical treatment of the sample. The task of carrying out spectral determination of uranium in rocks, etc., up to at least 0.005%, without preliminary chemical separation and concentration was not abandoned, however.

The investigations, described briefly below (Ivanov), showed that the best line of all those studied (4241.7 Å; 4090 Å and others) is the uranium line at 4361.69 Å as compared with the lines at 4090 Å, 4244 Å and 4241 Å, which were used by other workers. The main advantage of this line is

Table II. Comparison of the Sensitivity of the Methods

Elements	*Method of evaporation (%)*	*Scribner and Mullin's method (%)*
B	5×10^{-6}	8×10^{-6}
Mn	1×10^{-5}	1×10^{-4}
Co	5×10^{-5}	1×10^{-4}
Ni	1×10^{-4}	2×10^{-4}
Li	2×10^{-6}	5×10^{-5}
Cr	2×10^{-5}	3×10^{-4}

Table III. Results of Boron Determination in Uranium from Different Batches

Concentration of boron in weight % × 10^5

No. of batches			
120	*207*	*161*	*262*
4.8	2.1	2.4	3.1
6	3.0	2.2	3.1
5	2.8	3.0	3.4
5.5	2.7	2.4	2.4
4.7	2.2		
5.5	2.6		
4.0	2.3		
6.5	2.6		
	2.5		
Average 5.2	2.5	2.5	3.0

the absence of interference from atomic lines of other elements. The nearest line is Zr 4341.39 Å. In the case of the 1300 cm, autocollimating, three-prism glass spectrograph (ISP-51A); this line does not interfere with the determination of uranium which was carried out using the method of three etalons and absolute intensities.

In this analysis we used carbon electrodes into whose cavity (10 mm) we placed a sample which burnt out completely in the arc within 7 minutes. An example of the measurement is given in Table IV. For photographing the spectra 10,000 XD film was used; the spectra were measured with a microphotometer.

We studied in detail the influence of the associated chemical elements Al, Si, Fe, Ti, Mn, Pb, Cu and others. For rocks of similar composition the method made it possible to determine the contents of uranium up to 0.001%. In practice, the method was used to determine uranium up to 0.005%. The average value of the reproducibility of the determination was of the order ± 4–5%.

Table V shows the results obtained using this method for the analysis of U in rocks and compares these results with those obtained by chemical determinations on the same samples.

However, a more universal method of spectral analysis of uranium in various products proved to be by the method of adding to the sample, light isotopes of uranium, as internal standards.

METHOD OF ADDED ISOTOPES IN THE SPECTRAL DETERMINATION OF URANIUM IN ORES AND PRODUCTS

It is well known that the spectral line intensity of the elements constituting a sample to be analysed depends to a considerable extent on the total chemical composition and of the presence in it of additional components. This limits the universal applicability of spectroscopic methods of analysis and makes them unsuitable for direct utilization in the analysis of substances with varying chemical composition, even in the absence of those elements whose lines overlap those of the element that is being determined. For this reason the solution of problems of spectrochemical analysis requires a special experimental study of the influence of additional components in the sample on the results of the quantitative analysis. For obvious reasons it is absolutely necessary to account for this when working with samples of complex composition, for example, ores and rocks.

One of the most radical methods of minimizing the influence of additional components on the results of spectrochemical analysis and of increasing its precision and universality is the utilization of the isotopes of the element under analysis as an internal standard. The great similarity between the chemical and physical properties of the isotopes of the element under analysis permits one to predict that the isotope introduced into the sample will in all cases follow the principal isotope of the element under analysis. Under these conditions, the relative intensity of the lines of the two isotopic components will depend only to a minimum degree on the changes in the evaporation conditions during excitation of the atoms of the elements in the source, and will be determined mainly by the relative concentration of the isotopes in the sample.

The use of this method eliminates the necessity for the three etalon method and that, together with the increase of the precision in determination, makes it considerably more rapid.

It is known many lines in uranium show considerable isotopic shifts. These isotopic shifts were used for the quantitative spectral determination of uranium in various substances by introducing either the isotope U^{235} or isotope U^{233}, or both of them together, into the sample.

We systematically studied the spectra of U^{235} and U^{233}, chiefly in the region between 3900–4600 Å which is the richest in strong uranium lines; for this purpose we found the spectrograph ISP-51 (with camera $f = 85$) suitable since it resolved the isotopic structure of these lines. The results of such investigations made the practical utilization of the method possible for production control.

We found many lines of uranium with isotopic shifts of from 0.08 to 0.36 Å. The most useful line found for analytical purposes was at 4244 Å (shift = 0.23 Å). (See Fig. 3 and 4.) One of the known disadvantages is the overlapping of a tungsten line. In practice, however, tungsten is not encountered in quantities that may alter the relative intensity of the lines. The close similarity of the physical and chemical properties of U^{238}, U^{235} and U^{233} made it possible to predict that their conduct in the process of evaporation and excitation would be similar. The study of the evaporation curves (in an arc) of U^{235} and U^{233} from samples having different composition showed their similarity. It was further demonstrated that the relative intensity of the isotopic lines depended on the electrode size, the amount of the weighed sample, the change of current strength, etc. (see Table VI).

All this presents very great advantages over other known methods of the spectral determination of uranium. It was found to be sufficient to determine uranium in only one sample into which we introduced the isotopes. The precision of the determination was 3–4%, i.e., in this respect it rivalled chemical analysis. Precision could have been increased still

Table IV. Reproducibility of the Intensity Measurement of Line 4241.7 Å of Uranium

Uranium content, %	*Line 4241.7 Å*			
	1st spectrum	*2nd spectrum*	*3rd spectrum*	*Average*
0.02 Stand.	23.0	22.0	23.0	22.8 + 0.1 (1%)
0.01 Stand.	16.4	15.6	19.0	17.0 + 1.3 (8%)
0.0075 Determ.	15.6	13.8	16.8	15.4 + 1.0 (7%)
0.005 Stand.	11.9	14.5	15.2	13.8 + 1.3 (9%)
0.001 Stand.		12.5	11.6	12.0 + 0.3 (3%)

Table V. Comparison of Spectral and Chemical Determination of U

Sample	*Uranium found, %*		*Difference, %*
	Chemical determination	*Spectral determination*	
K-O	0.0075	0.0078	4
V-82	0.0093	0.0078	16
S-1	0.0075	0.0070	7
V-39	0.0071	0.0067	6
B-116	0.0080	0.0079	1

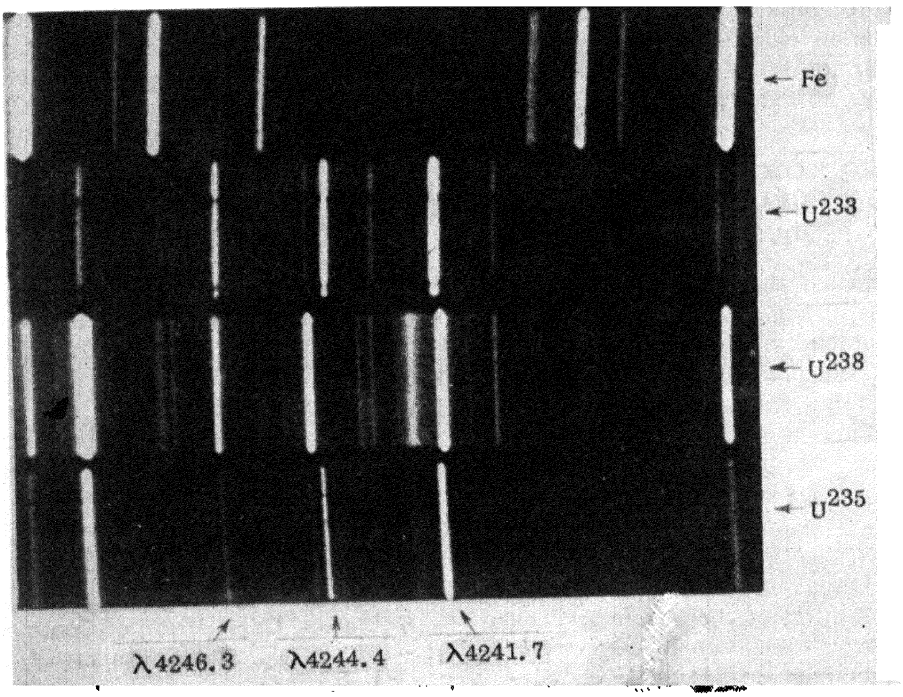

Figure 3. The isotopic shift of the uranium line 4244.4Å (isotopes U^{238}, U^{235}, and U^{233})

more by simultaneously introducing two isotopes into the sample, U^{235} and U^{233}.

The determinations were carried out on a number of samples having uranium contents ranging from 1% to 0.005% U.

A specific quantity of the light isotope of uranium was introduced into the sample and after thorough mixing the sample was arced.

Determination of the relative intensities of the isotopic components of the uranium line was carried out as follows. The spectrum was photographed using a nine-step platinum sector. For each isotope a separate density curve was constructed. These curves were used to find the relative intensity. Table VII shows the reproducibility of data. It should be noted that the structure of the lines of the isotopes U^{235} and U^{233} is hyperfine. However, the hyperfine structure of the 4241 line is not observed at the arc voltage used or by the prism spectrograph, in other words, we dealt essentially with a single line. Later on, it is proposed to prove the absence of any noticeable influence of the hyperfine structure on the relative intensity of the components (we have analytical purposes in mind).

The concentrations of U were calculated according to the following formula

$$x\,\% = \frac{I^{238} - I_B^{235}}{I^{235} - I^{238}} C^{235} - C^{238\prime}$$

where I^{235} and I^{238} corresponded to the intensity of the isotopic components, I_B^{235} is the background measured on the side of the light component at a distance of $\Delta\lambda = \lambda^{238} - \lambda^{235}$, while I_B^{238} is the background measured on the side of the normal U^{238} component at a distance of $\Delta\lambda$. C^{238} is the content of U^{238} introduced into the sample along with the light isotope. It should be noted, however, that measurement of the background is not very exact (although sufficiently to carry out determinations with precision up to 3–4%).

When necessary this can be avoided completely by simultaneously introducing as internal standard, the isotopes U^{235} and U^{233}. In this case measurement of the background is not required. In practice, the background can be eliminated in a number of cases by photographing the spectrum with different exposures.

Table VIII gives some idea of the precision of determination using this method. Compared with chemical determination, numerous analyses showed that every 10 mg of sample required $\sim 1 \times 10^{-6}$ gm of U^{235} and U^{233}, i.e., for 250 analyses of uranium there must be ~ 1 mg of the light isotope.

Table VI. Influence of the Electrode Size and the Amount of the Weighed Sample on the Determination of U

Carbon electrodes		Weighed sample, mg	Found U^{235}, %
ϕ	Depth, mm		
3	6	40	0.035
3	2	13	0.036
2	7	10	0.038

X-RAY SPECTOGRAPHIC METHOD FOR THE DETERMINATION OF URANIUM AND ITS ADMIXTURES

The X-ray spectrographic method of obtaining pure uranium has made possible the solution of the problem of determining a number of neutron-active rare-earth elements (Gd, Eu, etc.) in uranium which contained $\Sigma_{r.e.} \sim 10^{-5}\%$. On the other hand, it has also proved useful in determining uranium in uraniferous uranium-thorium and other minerals. As is known, a peculiar feature of this method is the relatively small influence which differences in the bulk sample composition and the presence of additional components have on the results of the analysis. In this paper I am not able to dwell on this at length. I will say, however, that this method has been well developed in the Soviet Union and is being successfully utilized in determining many elements, among them Nb, Ta, Zr, Hf and others. This method has also enabled the solution of a number of theoretical problems connected with the study of the energy structure of chemical compounds and solids. These researches are based on the study of the fine structure of X-ray spectra (Vainshtein and others).[5]

Bearing in mind analytical purposes, I would like to dwell on the construction of a number of new models of X-ray spectrographs and say that in the Soviet Union special attention is paid to the construction of focussing spectrographs with curved crystals of large sizes — 40 to 50 mm, for the vacuum and non-vacuum regions of the spectrum, with photographic and photoelectric recording of spectra. As is known, the quantitative determination of the contents of individual rare-earth elements in mixtures of same by methods of optical spectral analysis is encountering a number of difficulties and cannot be carried out with adequate precision for all elements. By contrast the same problem is relatively easily solved by the X-ray spectral method. As proved by experiments, all these elements, in any combination, can be determined quantitatively with an accuracy of 4–6%, provided their concentrations in the mixture are greater when 0.1%.

Unfortunately, in determining admixtures of the elements it is often necessary to concentrate, or, better to isolate the rare-earth elements from the metal. This, for instance, is necessary in the case of uranium. As a result of the application of various

Table VII. Reproducibility of U Data

$\frac{C_{238}}{C_{235}}$	*Deviation from average*
0.294	0.001
0.291	0.002
0.293	0.000
0.306	0.013
0.286	0.007
0.330	0.037
0.280	0.013
0.271	0.022
0.283	0.010

Average 0.293 ± 0.011 (3%)

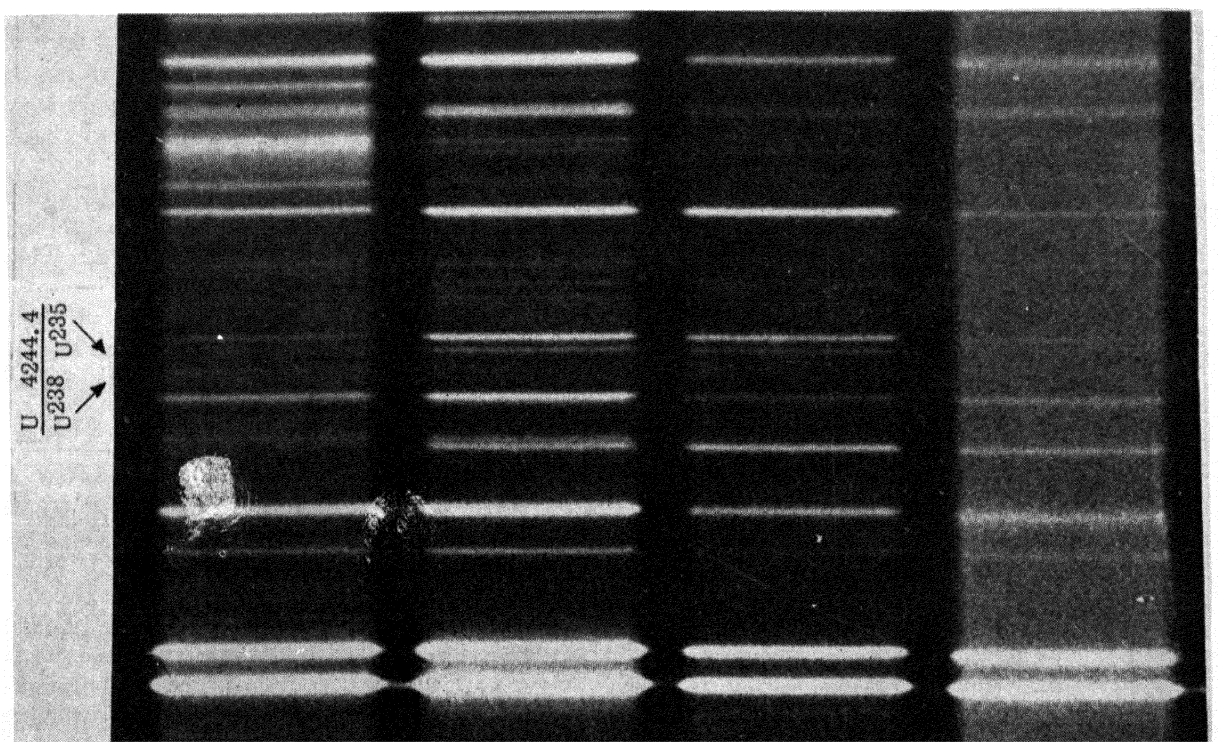

Figure 4. Isotopic components of the analytic uranium line 4244.4 Å in the spectrum of an ore sample

methods of separating total rare earths from uranium (based on the different reactions between the rare earths and U with HF, sulphates or bicarbonates, etc.), such methods have been developed. Ce was used as a carrier. The method was checked using radioactive indicators. Such a combination of chemical and X-ray spectral methods enabled us to determine total rare earths up to 10^{-7} gm. The quantitative X-ray-spectral determination of the rare-earth elements was carried out using the L–series of lines (usually using the most intensive $L\alpha_1'$, and $L\beta_1'$ lines) with the help of a vacuum focussing X-ray spectrograph with a radius of curvature ~ 500 mm and a quartz crystal with reflecting plane surfaces (10$\bar{1}$0). If during the course of analysis it was essential to determine the intensity ratio of the lines, we used both the Hevesy method and methods based on the use of the shape of the X-ray spectral lines. The major quantity of rare-earth elements isolated from uranium by the carrier cerium oxide were analysed to determine the content of one of the oxides, usually Nd. Since in the process of isolating these elements their relative concentrations did not change, the ratio of Nd_2O_3 to the sum of the oxides of the other rare-earth elements isolated from uranium, was known. Knowing this ratio and the experimentally estimated amount of Nd_2O_3 in the oxides isolated from uranium, it was possible, to determine the contents of all other rare-earth elements and the total. This method was widely used to determine the rare-earth and other elements.

POLAROGRAPHIC DETERMINATION OF URANIUM

The method of polarographic determination was widely used in the quantitative determination of uranium, present in small quantities in various substances.

The correct selection of conditions for the polarographic determination of uranium required the knowledge of the mechanism of reduction (or oxidation) of uranium on the dropping mercury electrode and solid electrodes. As is known, a number of researches dealing with this have been published.[6]

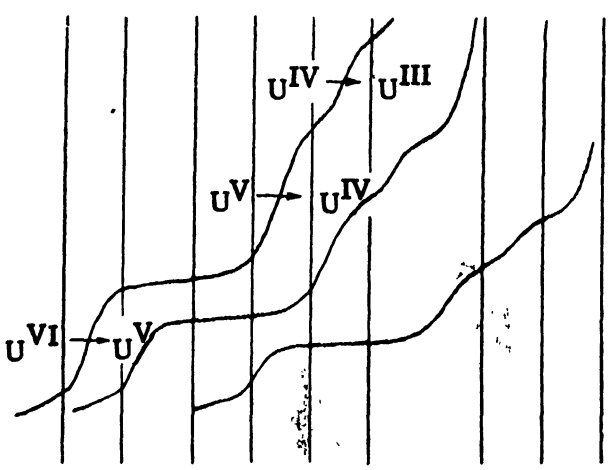

Figure 5. Three waves of uranium in solution of H_2SO_4 1×10^{-5}M + thymol 2×10^{-4}% (at different sensitivities)

Table VIII. Comparison of the Results of the Determination of Uranium by Chemical and Spectral Methods

Uranium found (%)		*Difference (%)*
Chemical determination	*Spectral determination (method of adding isotopes)*	
0.037	0.036	3.0
0.29	0.31	7.0
0.100	0.092	10.0
0.040	0.039	2.5
0.18	0.18	–
0.024	0.025	4.0
0.100	0.098	2.0
0.30	0.31	3.0
0.40	0.39	2.5
0.50	0.51	2.0
0.60	0.58	3.0
0.29	0.29	0.0
0.29	0.28	3.0
0.32	0.31	3.0
0.36	0.35	3.0
0.50	0.56	11.0
0.50	0.54	8.0
0.64	0.60	6.0
3.28	3.24	1.3
4.53	4.63	2.2
2.11	2.16	2.3
3.53	3.43	3.0
5.08	5.12	0.8
5.15	5.06	1.7

There are still contradictory opinions of the reduction mechanism of uranium. We shall dwell on this question only to speak of the researches that have been carried out in the Soviet Union.

In acid medium UO_2^{2+} produces one, two or three waves, depending on the value of the pH of the solution and the nature of the acid (see Fig. 5). In moderately acid solutions (pH = ~ 1–2) the uranyl ion produces two waves; $E_{1/2}$ of the first wave is = ~ −0.20 v (vs S.C.E.) and $E_{1/2}$ of the second wave is = ~ −0.90 v, the latter wave under these conditions being twice the height of the first.

Plotting for the first wave, log $(i/id) - i$ against E gives a straight line with a slope of 0.060 v. Subsequent determination of the ionising currents of UO_2^{2+} and Pb^{2+} of similar molarity from the same solution showed that $id\ Pb^{2+}/id'\ UO_2^{2+} = \sim 2.2$, and $id\ Pb^{2+}/id''\ UO_2^{2+} = \sim 1.1$.

Microcoulometric determination of the number of electrons (n) showed that there are three electrons taking part in the reduction process of uranyl ion. Many other observations of the changes in the height of the first wave, its shift, depending on the changes in the electrolyte, etc. (in agreement with many

authors[7]), show that the first reduction stage of UO_2^{2+} proceeds reversibly and corresponds to one electron reduction to the + 5 state and the reaction is

$$UO_2^{2+} + e \rightleftarrows UO_2^{+}$$

The condition of ions in the subsequent reduction stages of UO_2^{+} remains debatable. It seems that this is connected with the inadequacy of knowledge on the nature of hydrolysis, particularly of the ions U^{4+} and U^{3+}, although it is well known that U^{4+} and U^{3+} hydrolyze easily even in acid solutions. For this reason some investigators believe that the reduction process of UO_2^{+} in neutral and weak acid solutions proceeds with the formation of a solid film of UO_2 at the electrode surface which dissolves with the increasing acidity. Others believe that in sufficiently acid solution $4H^{+}$ participates in the recovery of UO_2^{+} and that the process is attended by the formation of U^{4+} and then of U^{3+}, and that in weak acid solutions the UO_2^{+} reduces to form bivalent ions of the type of $U(OH)_2^{2+}$ or UO^{2+} is more probable (Frumkin and Zhdanov).

In our experiments, the wave, corresponding to the stage $U^{4+} + e \rightleftarrows U^{3+}$, was reversible under certain conditions and this is accepted by many other scientists. In very strongly acid media the reduction stage $UO_2^{2+} \rightarrow UO_2^{+}$ disappears since the UO_2^{+} that forms is instable and immediately disproportionates and for this reason the first wave corresponds to two electron reduction, i.e., the process goes from UO_2^{2+} to U^{4+}.

The nature of the process of $UO_2^{+} + e \rightarrow U^{4+}$ reduction is in close connection with the process of the UO_2^{+} disproportionation and the rate, etc., which are different in different media. As to the oxidation of U^{4+}, as far as is known no anode wave for U^{4+} has been obtained using the dropping mercury electrode. However an anodic wave U(IV) oxidation to U(VI) with $E_{1/2} = 1.046$ v (hydrogen electrode) was obtained with a rotating platinum electrode. The mechanism of the anodic oxidation of U^{4+} is very complicated because the oxidation reaction of U^{4+} by oxygen isolated electrochemically on Pt (Vesselovsky and Rosenthal) is superposed on the electro-chemical oxidation reaction of U^{4+}.

In practical polarography, in particular in the process of quantitative uranium determination, we generally made use of the first wave. The potential of the half-wave of the first stage $UO_2^{2+} + e \rightarrow UO_2^{+}$ depends only slightly on pH and only in strong acid solution is somewhat shifted towards more negative values because of the formation of complex ions. The first wave increases with increasing acidity and reaches double height in 1–2 *M* acid solutions, which is profitable for the sensitivity increase. However, the polarographic determination of uranium in acid media indicates the absence of a number of elements which interfere with the determination of uranium. The main difficulty in practical polarography is the influence of a number of elements on the diffusion current of uranium and the necessity to find means of eliminating them.

Below we give examples of the direct polarographic determinations of uranium in various products in the presence of various elements after dissolving them without any chemical separation or concentration. As to the methods of quantitative polarographic determination of uranium with a preliminary chemical preparation, i.e., with the isolation of interfering elements, they are in great variety and many of them have been successfully used in practical work. They demand considerable time, however. Uranium loss is also possible in the process of separation of uranium from other elements. In the direct determination of uranium in samples, the influence of the interfering elements was eliminated by selecting suitable electrolyte and by the use of complexing either for interfering the elements for

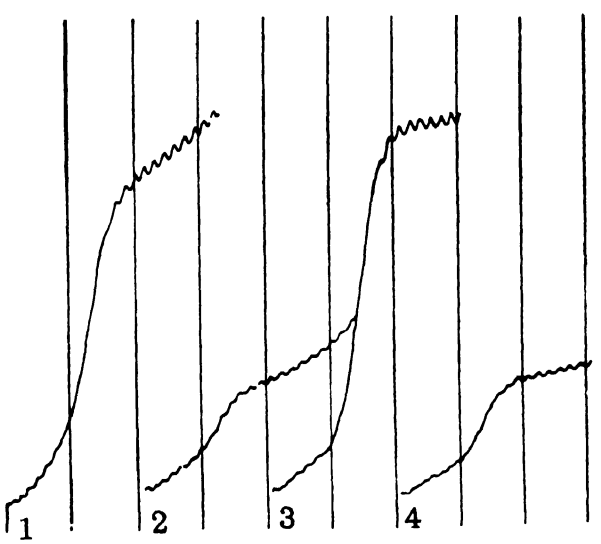

Figure 6. Influence of vanadium on diffusion current of UO_2^{2+} in lactic acid: (1,3) diffusion current of uranium in the presence of vanadium; (2-4) diffusion current of uranium without vanadium

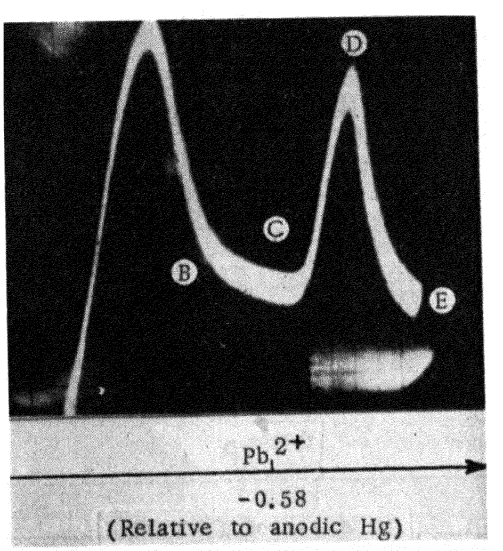

Figure 7. A typical oscillogram (Pb^{2+} in 0.024*N* HCl solution): (A,B) condense current; (C,D,E) diffusion current Pb^{2+}

the uranium (Sinyakova). There are numerous researches, but we shall deal only with the determination of uranium in the presence of Fe, Ti, Cu, V, Mo and others without chemical preparation of the sample.

For the Fe^{3+} reduction we used ascorbic acid and hydrazine sulphate. The latter has the advantage of precipitating Cu^{2+} simultaneously with the reduction of Fe^{3+} and forms on boiling with copper ions the compound $Cu(SO_4)(N_2H_5)_2SO_4$. In solutions of hydrazine sulphate. UO_2^{2+} gives a well-expressed wave with $E_{1/2} = -0.20$ v (vs. S.C.E.) for which linear dependence between diffusion current and the uranium concentration in solution is maintained. V, Mo and Ti interfere with the determination of uranium in hydrazine sulphate. Vanadium offers the greatest difficulties in the determination of uranium by any method. However, lactic acid, used as the electrolyte in the polarography of uranium makes it possible to determine small amounts of uranium in the presence of a large excess of vanadium. In addition, vanadium exerts a positive influence since it increases the sensitivity of the polarographic determination of uranium almost five times (see Fig. 6).

In a lactic acid medium the linear dependence between diffusion current and uranium concentration in solution is maintained and thus permits the use of this electrolyte in the quantitative determination of uranium. In lactic acid, the modybdenum wave is shifted towards more negative values as a result of complex formation and therefore, it does not interfere in the determination of uranium.

In order to eliminate the influence of Ti, chromotropic acid is added to lactic acid which binds Ti in a complex and Ti does not interfere in the uranium determination.

Fe^{3+} and Cu^{2+} interfere in uranium determinations in lactic acid media. For this reason in determining uranium we made use of a combined electrolyte: lactic acid + hydrazine sulphate in which uranium can be determined immediately after the sample is solved (see Table IX).

Table IX. Results of Ore Analysis

No. of experiment	Uranium found, %	
	In a background of hydrazine sulphate-lactic acid after dissolution	In a background of hydrazine sulphate after ether extraction
1	0.053	0.055
2	0.059	—
3	0.055	0.054
4	0.053	0.053
5	0.054	—
6	0.054	0.055
Average	0.055	0.054

At the same time, polarographic determination of uranium was very often combined with some chemical preparation, but will not be discussed here.

OSCILLOGRAPHIC POLAROGRAPHY OF URANIUM

This method has a number of variants and has been worked out in the past few years. Its main advantage over the normal polarographic method is that it is more sensitive by an order of 1.5, i.e., it is possible, for instance, to determine uranium in concentrations $\sim 10^{-6}\%$ with a precision of $\pm$ 5%.

In principle, the method works as follows: the plates that deflect the ray of the oscillograph cathode-ray tube in a horizontal direction are supplied with saw-tooth wave voltage, proportional to the voltage passed on to the polarographic cell. The plates that deflect the rays vertically, are supplied with voltage that is proportional to the current passing through the cell. Thus, a volt-ampere curve, the form of which corresponds to the one shown in Fig. 7 appears on the screen of the cathode-ray tube.

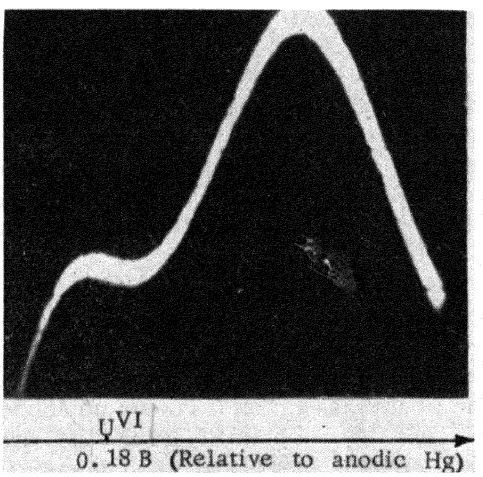

Figure 8. The first wave of uranium in 0.024N HCl solution

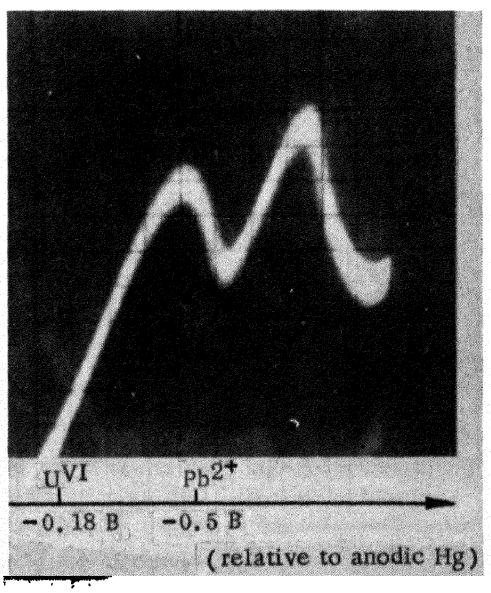

Figure 9. Two waves of uranium in 0.024N HCl solution

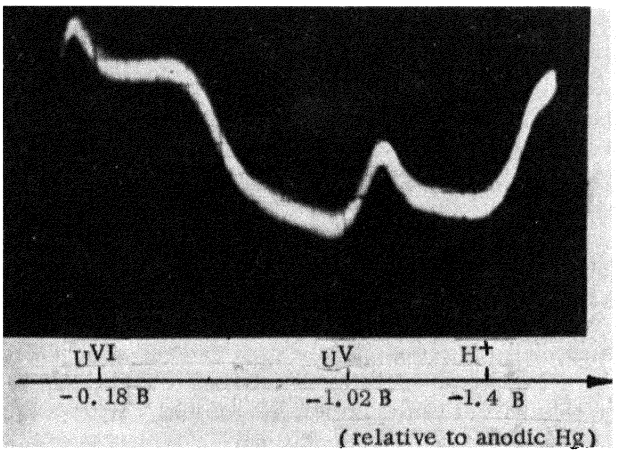

Figure 10. The wave Pb^{2+} in the presence of a large amount of uranium

The height of the voltage at which the current begins to increase sharply (C) characterizes the nature of the substance in solution. A further increase of potential in the electrolytical cell leads to an increase of the current passing through the electrolyte, to a certain maximum value. The maximum height of current (D) characterizes the concentration of the substance in solution. The value of the maximum current depends on the rate of variation in the change of the saw-tooth wave voltage which is passing into the cell, and this in turn, depends on the purity of the sweep generator and the value of the amplitude of the saw-tooth wave voltage.

The product of these values gives the rate of change of the saw-tooth wave voltage passing into the cell. The results obtained can be compared only at a continuous velocity of rate of change of potential.

These experiments were carried out with the aid of an oscillographic polarograph constructed in the Soviet Union (Gokhshtein).

We have also studied the mechanism of the UO_2^{2+} reduction and worked out the conditions for determining a number of element admixtures simultaneously with the uranium determination. In oscillographic polarography we discovered two waves in different media, with one wave corresponding to the reduction potential = —0.18 —0.2 v (see Fig. 8), and the other wave (obviously, a summation) = —0.9 —1.0 v (see Fig. 9).

The reduction wave $U^{4+} \rightarrow + e \rightarrow U^{3+} = \sim$ —1.02 v (in 0.02 N HCl solution). Analysis of the first wave (in particular, using equation by Sevćik[7]), showed that it corresponds to the reversible process, while the second corresponds to the irreversible.

In practice, this method was used, for instance, to determine U and Pb when present together in uranium minerals (see Fig. 10). This is important in determining the absolute geologic age of minerals with the uranium-lead method. Comparison of the methods of determining Pb oscillographically–polarographically, colorimetrically and by electrochemical precipitation, has shown the advantages of the oscillographic polarographic method.

At the same time we have successfully determined the contents of U in minerals (Zhirova).

The physical and physico-chemical methods of analysis conducted in conjunction with other methods, particularly chemical methods, that I have described briefly in this paper, have ensured adequate control over uranium production.

These methods, however, are also of interest for other fields where they were utilized successfully.

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The Analysis of Low-Grade Uranium Ores and their Products

By M. D. Hassialis and R. C. Musa,* USA

The investigation of ore-dressing processes for the beneficiation of low-grade uranium ores requires the routine analyses of solids containing 0–10 micrograms of uranium per gram of sample and of solutions containing 0–10 micrograms per milliliter. When these analyses are used in the evaluation of the over-all performance of some proposed treatment scheme, the requirement that the uranium satisfies a mass balance imposes an additional limitation on the variance due to analytic procedures.

FLUORIMETRIC METHOD

Of the various methods available for the analysis of uranium, the fluorimetric method has been most frequently adopted as the basis for routine analysis. The routine procedure developed by Grimaldi and his co-workers[1,2], leads to satisfactory results with samples in the intermediate- and high-concentration ranges, but not in the low end of the concentration range. By means of the modifications discussed below the fluorimetric method can give routine analyses with an absolute accuracy of 97% of the contained uranium and a standard deviation of under 3.5% in the low-concentration range.

Procedure

The detailed procedure is as follows: A 200 mg, —60 mesh sample is weighed into a 30 ml Pt crucible and ignited at 600°C to remove organic matter; 10 ml HF and 10 ml of 50 vol % HNO_3 are added, the sample is digested on a steam bath for one hour and then evaporated to dryness. Fluoride is removed by evaporation with 50 vol % HNO_3, whereupon sample is dissolved in this acid and transferred to a volumetric flask where HNO_3 concentration is adjusted to 10 vol %.

One of two procedures is now followed to remove elements which interfere by quenching uranium fluorescence. When the sample contains more than 0.01% U, a 1 ml aliquot of the sample is put in a 30 ml, glass-stoppered test tube and 10 ml of a solution containing 5 vol % HNO_3 and approximately 900 gm/l of $Al(NO_3)_3 \cdot 9H_2O$ are added using a Filamatic Vial Filler. When the sample contains less than 0.01% U, a 5 ml aliquot of sample is placed in the 30 ml glass-stoppered test tube containing 9.5 gm of $Al(NO_3)_3 \cdot 9H_2O$. The tubes are placed in a specially designed 20-tube rack and the rack placed in a hot-water bath. The tubes are shaken intermittently until dissolution is complete when they are cooled to room temperature.

To the sample and aluminum nitrate solutions, 10 ml of ethyl acetate are added using a Filamatic Filler and the stoppered test tubes together with rack are transferred to an automatic shaker which agitates them for 5 minutes. The phases are then allowed to separate whereupon approximately 5 ml of the ethyl acetate phase is pipetted off and filtered through a dry, Whatman No. 42 filter paper self-supported in the neck of a test tube, thus removing any entrained water phase. A dense, cation-free paper gives best results. A 1 ml aliquot of filtrate is transferred to a Pt dish which has been placed in a holder so positioned that the bottom of the dish is immersed in cold water. To prevent loss by creeping, the ethyl acetate is immediately ignited by means of a small flame and allowed to burn off. The dishes are then placed on a hot plate held slightly above 100°C and residual water evaporated. The hot plate is a Lindberg Model H-2 fitted with an adaptor designed to hold 25 flux dishes ½ inch above the surface of the hot plate.

The flux used is that recommended by Grimaldi[1] containing 9% NaF, 45.5% Na_2CO_3 and 45.5% K_2CO_3 by weight. It has been found satisfactory for buttons containing as little as 0.005 micrograms of U; the blank reading from these buttons being equivalent to that from 0.002 micrograms of U. Two gm of flux are added to each dish and the dish is placed in a desiccator until ready for fusion. Fusions are carried out in a rocking furnace made by mounting a Timco Electric Furnace Model RCE on a New Brunswick Scientific Company Gyratory Shaker Model S-3. The dishes are mounted in a 3-tier stainless steel tray holding 5 dishes per tier and of over-all dimensions $5\frac{3}{16}$ in. × $4\frac{1}{4}$ in. × $2\frac{11}{16}$ in. which just fits the furnace fire box. The samples are held at 72°C for 5 minutes which is about 2 minutes longer than the melting time. The dishes are then removed and put in a desiccator where they cool for 1 hour before reading.

The use of a shaking, fluxing furnace is a new development. It replaces heating by hand in a Mecker burner at red heat for about 30 seconds in order to melt the flux and then maintaining the flux at just above its melting point for 90 seconds by keeping it in the flame intermittently while at the same time

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the dish is swirled to incorporate and distribute all of the uranium sample in the flux. Although the results obtained by a careful and experienced operator are reasonably good, the procedure is tedious, time consuming and subject to large variations. The furnace provides continuous swirling of the flux with good control of temperature and gives a great saving in time.

The fluorescence of the button is determined using a Model V Transmission Fluorimeter. The exciting ultraviolet light (3650Å) is obtained by filtering the light from a G.E. H100-E4, high-pressure, mercury-vapor lamp with two Corning No. 5874 filters each 5-mm thick. The emitted light is filtered by a system composed of Cornings No. 9780 and No. 3486 each 5-mm thick to give a peak at 5550Å. The resulting visible light is converted photoelectrically and amplified by a photomultiplier circuit using an RCA 5819 tube. The output current is read by an RCA Ultrasensitive D.C. Microammeter, Model WV-84A. To minimize the effect of chips from the buttons falling on the fluorescence filter a non-fluorescent glass is placed between the sample holder and filter. This glass is also used as a standard absorbence in adjusting the photomultiplier amplification to the same setting for all readings.

The uranium content of each button is obtained by comparison of its fluorescent intensity with that from buttons obtained from known solutions. Four knowns and eleven unknowns are run in each set of samples; the four standards being used as the basis for the calculation of the eleven unknowns. The uranium content of the standards is chosen so as to match, wherever possible, the estimated uranium content of the unknowns.

Study of Procedure

When the fluorimetric method failed to give routinely acceptable results in the low-concentration range, the contribution of the various steps of the procedure to the over-all variability of results was studied with the results described below.

Digestion Procedure

The HF-HNO_3 digestion was studied by giving a sample of each of two lots of shale to four operators who digested each sample to give the corresponding solutions which were then analyzed four times. The results are given in Table I.

The estimate of the variance between replicates on the same digestion is given by $\sigma^2 = 3(7.28 + 5.10 + 3.37 + 14.27)/12 = 7.51$ and has 12 degrees of freedom. The estimate of variance obtained by considering the means of the different digestions is given by $\sigma^2 - 4\sigma_\xi^2 = 4 \times 0.82 = 3.28$ and it has 3 degrees of freedom. If there were no contributions to the over-all variability from differences between the average values for the different digestions then $\sigma_\xi^2 = 0$ and the ratio of variances, F, would be distributed with 3 and 12 degrees of freedom. Hence the hypothesis that $\sigma_\xi^2 = 0$ can be tested by computing the variance ratio for different significance levels. For $F_{n1,\,n2,\,\alpha} = F_{3,\,12,\,0.05}$ value of 3.49 is obtained, while $F_{3,\,12,\,0.01} = 5.95$. The determined value is $F = 328/751 = 0.44$; hence the conclusion may be drawn that the variance between digestions is unimportant in the over-all variance. The same conclusion may be drawn for Lot II where $F = 0.36/14.88 = 0.03$. In practice routine analyses provide only for duplicate digestions to eliminate the possibility of any gross errors.

Extraction Procedure

The purpose of the ethyl acetate extraction is to separate the uranium from all possible interferences before preparing the final melt. The major interferences encountered are iron and relatively high sulfuric acid concentrations. Other interferences are either removed completely by extraction or are not present in appreciable quantities in the samples.

Table I. Results of HF-HNO_3 Digestion

Lot no.	Operator 1	2	3	4
I	79.3	78.1	79.4	82.6
	84.7	80.9	79.7	79.1
	78.7	80.0	82.6	83.2
	80.9	75.8	78.3	75.0
$\bar{x}_i$	$\bar{x}_1 = 80.9$	$\bar{x}_2 = 78.7$	$\bar{x}_3 = 80.0$	$\bar{x}_4 = 80.0$
σ_i^2	$\sigma_1^2 = 7.28$	$\sigma_2^2 = 5.10$	$\sigma_3^2 = 3.37$	$\sigma_4^2 = 14.27$
II	85.3	93.1	87.5	93.9
	90.9	95.0	94.4	92.0
	89.6	89.8	89.2	89.2
	97.6	84.8	90.7	89.5
$\bar{x}_i$	$\bar{x}_1 = 90.9$	$\bar{x}_2 = 90.7$	$\bar{x}_3 = 90.5$	$\bar{x}_4 = 91.2$
σ_i^2	$\sigma_1^2 = 25.98$	$\sigma_2^2 = 19.96$	$\sigma_3^2 = 8.65$	$\sigma_4^2 = 4.94$
$\bar{x}_I = 79.9$,	$\bar{x}_{II} = 90.8$			

The presence of large amounts of iron in a sample can usually be overcome by dilution before extraction, since only very large iron to uranium ratios are troublesome. Table II shows the effect of large amounts of ferric iron on readings obtained for a solution containing a known U concentration and no foreign anions (i. e., only NO_3 present). Each readings is the average of 4 independent determinations.

Table II. Interference by Iron

U conc. (γ/ml)	*Fe conc. (mg/ml)*	*Average reading*	*% error*
2.0	0	79	0
2.0	0.5	79	0
2.0	2.0	76	−4
2.0	5.0	62	−20
0.02	0.05	80	−1

It can be seen that at iron concentrations around 2.0 mg/ml, sufficient iron is carried into the ethyl acetate solution to result in quenching of the fluorescence of the uranium in the button. In a solution containing 2 micrograms/ml of U and 5 mg/ml of Fe, a 20% error results. However, by diluting this solution one-hundredfold (last line in Table II), the interference is eliminated. Since 0.01 micrograms/ml is the lower limit for good results using the simple mixed flux, and since 2 mg/ml of Fe is the upper limit on the tolerable iron concentration, any sample in which the iron-to-uranium ratio exceeds 2×10^5 must be given special treatment.

Interference by sulfuric acid is marked at high concentrations. Increasing the acidity of a standard solution decreases the reading obtained even if no foreign anions are introduced. The introduction of sulfate ion makes this effect even more marked. The readings obtained for standard U solutions containing various concentrations of HNO_3 and H_2SO_4 are summarized in Table III. Each value is the average of at least three determinations.

These results show clearly that increased acidity leads to lower readings, and that the presence of sulfate causes lower readings. The effect of nitric acid is probably due both to a change in the distribution coefficient of uranyl nitrate between water and ethyl acetate and to alteration of the mutual solubilities of these two phases. The sulfate action is probably due to the complexing of UO_2 as $UO_2(SO_4)$, $UO_2(SO_4)_2^=$, $UO_2(SO_4)_4^{6-}$, etc. These complexes compete with uranyl nitrate. In the routine procedure all high acid samples are diluted prior to extraction to less than 1 vol %. Where this is not possible neutralization or elimination by fuming is used to reduce the acidity and sulfate concentrations.

The large amount of aluminum nitrate is used to assure formation of extractable uranyl nitrate and to provide an excess of aluminum to complex such anionic interferences as sulfate and phosphate.

Since the use of solid $Al(NO_3)_3 \cdot 9H_2O$ entails warming in order to dissolve the solid and subsequent cooling before extraction, several experiments were performed to determine whether a nearly-saturated aluminum nitrate solution could be substituted. In each experiment the total aqueous volume was 11 ml, composed of 1 ml of a 1 microgram/ml U solution, x ml of a 900 gm/l $Al(NO_3)_3 \cdot 9H_2O$ solution containing 10 vol % HNO_3 and $(10 - x)$ ml of a pure 10 vol % HNO_3 solution. Each aqueous solution, therefore, consisted of 11 ml of 10 vol % HNO_3 containing 1 microgram of U and various quantities of aluminum nitrate. Each solution was extracted with 10 ml of ethyl acetate, the ethyl acetate was filtered and at least two aliquots from each ethyl acetate phase were evaporated, hand-fluxed and read. The readings obtained are shown in Table IV.

Table III. Effect of Acidity and SO_4 on Readings Obtained

U (γ/ml)	*Acid medium*	*Average reading*
2.0	H_2O	91
2.0	1.6*N* HNO_3	84
2.0	3.2*N* HNO_3	75
2.0	4.0*N* HNO_3	66
2.0	8.0*N* HNO_3	55
2.0	4.0*N* HNO_3 − 4.0*N* H_2SO_4	51
2.0	2.0*N* HNO_3 − 6.0*N* H_2SO_4	33
2.0	8.0*N* H_2SO_4	27 very erratic

Table IV. Effect of $Al(NO_3)_3$ Concentration on Uranium Extraction

ml Al solution	*ml 10% HNO_3*	*Average reading*	*No. of extractions*	*Standard deviation of extractions*
5	5	65.0	1	—
6	4	75.5	1	—
7	3	79.5	1	—
8	2	82.3	7	2.5%
9	1	84.5	7	2.5%
10	0	85.1	6	2.8%

Since in the region 9–10 ml of $Al(NO_3)_3 \cdot 9H_2O$ solution, the effect of slight changes in the aluminum nitrate concentration is very small, and since excellent precision was obtained throughout these experiments, the use of aluminum nitrate solution was adopted for all samples from which a 1 ml aliquot supplied sufficient uranium for satisfactory measurement (at least 0.05 micrograms of U).

The possibility that the extraction efficiency might depend upon the uranium concentration was also investigated. Solutions containing varying amounts of U were extracted using 1 ml of solution, 10 ml of aluminum nitrate solution and 10 ml of ethyl acetate. Each solution was extracted three times, and two aliquots from each extraction were evaporated and hand-fluxed. The readings obtained are given in Table V.

Thus the extraction efficiency appears to be independent of the U concentration in the range in which most of our samples were run. Comparisons with buttons prepared directly (without extraction)

Table V. Extraction Efficiency vs Uranium Concentration

U, γ/ml	1	0.5	0.2
1st extraction	82, 83	41, 41	16, 18
2nd extraction	77, 78	42, 42	17, 17
3rd extraction	80, 80	38, 41	18, 18
Average reading	80.0	40.8	17.3
Blank reading	1.5	1.5	1.5
Difference	78.5	39.3	15.8
Units/microgram U	78.5	78.6	79.0

Table VI. Effect of Filtration

Solutions	Reading
Extracted U–$CH_3 \cdot COO \cdot C_2H_5$	
1. Filtered once, Whatman No. 3 paper	57
2. Filtered once, Whatman No. 42 paper	59
3. Unfiltered	29
Unextracted U–$CH_3 \cdot COO \cdot C_2H_5$	68
1. Plus 0.1 ml unfiltered Al blank	58
2. Plus 0.5 ml unfiltered Al blank	39
3. Plus 1.0 ml unfiltered Al blank	32
4. Plus 1.0 ml filtered Al blank	67

from ethyl acetate-uranium solutions of known concentration indicate an overall extraction efficiency of about 90%.

Filtration

A study was made to determine the need for filtration. Standard uranium solution was extracted to give typical ethyl acetate solution. A uranium-free blank of aluminum nitrate was similarly prepared. An unextracted uranium solution in ethyl acetate of the concentration—the standard would have had if the extraction was 100% efficient was prepared. The comparisons are given in Table VI and indicate the need for filtration.

Evaporation

Three methods for removing the ethyl acetate from the final 1 ml aliquot have been studied; cold evaporation in a stream of air, which gives erratic results owing to the creeping of ethyl acetate, dropwise evaporation into a hot platinum dish supported on a small aluminum holder about ½ inch from the surface of the hot plate, and the burning technique previously described. Table VII gives a comparison of the precisions obtained by several operators using the hot evaporation and burning techniques. These results are based upon the readings obtained with the known uranium solution used as the calibrating standard for all routine analyses. The standard deviations given are based on results obtained during everyday routine operations. Hand-fluxing was used throughout.

It is evident that the burning technique is more precise, though in the hands of a skilled operator, as with No. 3, the hot dropwise evaporation can be as effective; the main trouble being spattering and carelessness arising from the tediousness of the procedure.

Fluxing

Variation in the amount of flux will cause a small variation in assay. Table VIII shows the effect of large changes in the weight of flux added to 0.1 micrograms of U.

Actual weighings on a series of finished buttons indicate variation from 1.9–2.1 gm. A button differing from 2.0 gm by 0.1 gm will be in error by 1.5%.

The mixed flux used in these analyses is prepared in batches of 6.7 pounds each. It has been found that different batches yield readings which differ from each other by as much as 10%. Since all unknowns are run together with standards, and the same batch of flux is used for both, no attempt has been made to determine the cause of this variation.

The hand-fluxing technique described previously has been used for all work until the recent development of the shaking-furnace procedure. The results obtained with hand-fluxing are quite satisfactory, but very time consuming. A standard deviation of 3–5% may be obtained in the routine analysis of both solids and solutions using burning and hand-fluxing.

Successful furnace fluxing depends upon proper swirling of the molten flux, maintenance of an optimal temperature and the elimination of thermal gradients within the furnace which give rise to variations between buttons of the same batch. The shaker previously described has a variable amplitude permitting variation of the degree of agitation. The interior furnace dimensions closely match those of the sample tray consequently temperature gradients appear, the worst of which is from back to front produced by the cooling of the front door when the furnace is opened. At high temperatures, e.g., above 750°C a marked top-to-bottom gradient appears. At temperatures below 700°C it is difficult to remove the sample tray and set it down on a level surface before premature solidification of the flux in the front dishes takes place. This causes a serious departure from the normal geometry of the buttons lead-

Table VII. Hot Evaporation vs Burning

Operator	Standard deviation: Hot dropwise evaporation	Standard deviation: Burning
1	4.2%	3.2%
2	4.9%	3.5%
3	2.9%	3.0%
4	3.9%	2.7%
5	5.9%	3.0%
6	4.0%	3.0%

Table VIII. Effect of Weight of Flux

Weight of flux (gm)	Average reading
1.5	92
2.0	86
2.5	80

ing to a dispersion of readings in the fluorimeter depending upon orientation of the button. Table IX gives the results obtained in a series of runs in which 1 ml aliquots of a standard solution of 0.1 micrograms/ml of U in ethyl acetate were used. The values given are the averages of six buttons for front to back and of five buttons from top to bottom.

These results show conclusively that the temperature range from 710–725°C with a time range from 4½–6 minutes gives only slight position-to-position effects and also gives consistently small standard deviations. Considering the fact that the seven runs at 725°C when combined give an over-all standard deviation for the evaporation and fluxing of 3% or better, it was decided to use 725°C for five minutes for routine operation. An estimate of the standard deviation of the procedure was calculated using the results obtained from duplicate analyses of 246 samples. The variance of each pair of duplicates was calculated, and these variances were used to obtain a population estimate of 4.0%.

The readings obtained for the daily standards with the furnace procedure indicate that at 725°C and five minutes there is a slight front-to-back effect, with the front being about 3% lower. Other time-temperature combinations are being studied in an attempt to decrease this difference. The possibility of using a furnace with a large fire-box is under consideration.

Reading

The most common source of error in reading the fluorimeter is the presence of flux chips either on the secondary filter system or on the clear glass provided as the protection for the filter system. Much of this difficulty has been overcome by using a vacuum cleaner to clean the sample holder and the clear glass. However, since the clear glass is used as a reference standard for setting the photomultiplier high voltage, it is desirable to have some independent standard for setting the photomultiplier amplification in order to be sure that the glass and the filter system are clean.

Most fluorescent standards have not proven practical.[3] Our experience has shown that the reading obtained for a normal button containing 1 microgram of uranium and stored in a desiccator does not change after several months of storage. Buttons containing 0.1 microgram of U change appreciably in a few days. In view of this, a 1 microgram button is used as our primary standard. The meter-setting procedure is as follows: (*a*) clean all glass thoroughly; (*b*) set high voltage so that clear glass standard gives a reading of 80 (on meter scale of 100 units); (*c*) place standard 1 microgram button in holder and read (The reading of this primary standard is arbitrary. The object of this procedure is to reproduce that reading each day.); (*d*) if the standard button reads incorrectly, clean all glass surfaces again, and re-set high voltage; (*e*) read standard button.

This procedure yields the same reading for the standard button day after day. After a time, of course, the photomultiplier tube or the ultraviolet light may change enough so that cleaning the instrument will no longer give the same reading for the standard button. In this case, the distance between the light and the button can be changed so as to obtain the correct reading for the standard button. Thus, a constant meter reading can be obtained at all times.

Conclusion

Routine fluorimetric analyses for uranium in a wide variety of materials can be accomplished rapidly and accurately using furnace fluxing. A single technician working an eight-hour day can analyze four sets of solutions, each consisting of eleven unknowns and four standards. (This does not include the digestion of solid samples.)

The standard deviation obtained from routine replicate analyses performed in this manner is almost always less than 5%. The accuracy obtained has been

Table IX. Time-Temperature Study in Furnace Fluxing

Temp.	*Time*	*Average reading*	*Standard deviation*	*Top*	*Bottom*	*Front*	*Back*
705	5½	90.0	5.2	94	85	87	92
705	6½	89.3	1.5	89	88	89	89
705	7	89.7	3.1	90	88	91	89
710	5	88.4	3.0	90	86	89	88
710	6	88.4	4.3	87	88	89	88
710	6	89.8	1.7	89	90	89	90
710	6	91.7	1.9	90	92	92	92
710	7	92.4	2.1	92	93	92	93
710	8	93.1	3.3	89	96	93	94
725	4	87.1	2.6	88	86	86	88
725	4½	88.1	1.2	88	87	88	89
725	4½	89.1	1.8	90	89	90	89
725	5	86.4	2.6	86	87	86	87
725	5	87.4	1.6	86	87	87	87
725	5	89.1	2.7	88	89	89	89
725	5½	87.6	2.7	87	87	88	88

checked using a mass spectrometric isotope dilution technique which will be described below. In all cases the values obtained fluorimetrically are within a few per cent of those obtained mass spectrometrically and there is no evidence of a bias in the fluorimetric analysis.

MASS SPECTROMETRIC ISOTOPE DILUTION METHOD

Procedure

An isotope dilution method for the determination of uranium has been described by Hess.[4] The procedure involves addition of a known amount of a uranium isotope, either U^{233} or U^{235}, and the measurement of the U^{238}/U^{235} or U^{238}/U^{233} ratio after spiking.

In our procedure the unknown solution is spiked with U^{235}. The uranium is extracted from the solution using ethyl acetate and $Al(NO_3)_3$ as the salting agent, if the unknown is in nitric acid solution (all solids are dissolved in HNO_3 as previously described) or, a solution of Armeen 2-12 (didodecylamine) in chloroform when the unknown is in sulfuric acid medium. The resultant organic phase is evaporated, ignited, if necessary, to remove any remaining organic matter, and the residue then taken up in a few drops of 10 vol % HNO_3. This solution is evaporated onto a tantalum filament (using infra-red heat) and the filament placed into the instrument. The isotope ratio is measured and the uranium concentration in the unknown calculated from the following:

$$R = \frac{XR_n\left[1 + R_y\left\{\frac{238}{235}\right\}\right] + YR_y\left[1 + R_n\frac{(238)}{(235)}\right]}{X\left[1 + R_n\right] + X\left[1 + R_n\frac{(238)}{(235)}\right]}$$

where, R = measured mole ratio U^{238}/U^{235}, R_n = mole ratio U^{238}/U^{235} in unknown (natural) sample, R_y = mole ratio U^{238}/U^{235} in spike (U^{235} enriched) solution, X = weight of U in unknown sample aliquot, and Y = weight of U in spike solution aliquot.

The instrument used is a 6-inch radius, 60-degree sector, double-focusing mass spectrometer similar to Nier's[5] except that a surface ionization (thermal emission) ion source[6] is used. The experimental instrument is capable of handling four samples per day. Construction of a more complex instrument incorporating a sample vacuum-lock assembly modeled after the one built at the Idaho Falls installation of the Phillips Petroleum Company[7,8] has been started. This instrument should be capable of handling fifteen samples per day since evacuation time is reduced to a few minutes per sample.

Results

The first results obtained were a series of replicate determinations designed to supply an accurate analysis of the U^{235} solution which would be used as the isotopic spiking solution. Eleven determinations were performed in the following manner: An aliquot of a gravimetrically standardized natural uranium solution was added to an aliquot of the U^{235} solution, the mixture was evaporated and placed on a filament and the ratio determined. The ratios (U^{238}/U^{235}) varied from 0.7 to 1.5. The standard deviation of the eleven results was 0.8%.

As a check on the accuracy of the fluorimetric method, several samples which had been analyzed fluorimetrically were analyzed using the isotope dilution technique. The comparisons obtained are given in Table X. These results show the excellent agreement that is usually obtained with the two methods. In practice, the isotope dilution technique is used for samples which require very accurate analysis, e.g., tailings from an ore-dressing process.

Table X. Comparison of Fluorimetric and Isotopic Dilution Analyses

Sample description	*U-fluorimetric*	*U-isotopic dilution*
Shale sample 1	0.00799%	0.00801%
Shale sample 2	0.00908%	0.00910%
Shale sample 3	0.00803%	0.00820%
Roasted shale	0.0110%	0.1018%
Unidentified solid	0.53%	0.54%
H_2SO_4 leach solution	31.1 μg/ml	31.9 μg/ml

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The Application of Analytical Chemistry to the Study and Evaluation of Uranium Minerals

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The problems encountered in analytical chemistry in connection with the evaluation of uranium ores are not widely different from those found in other routine operations of a similar type.

In fact, uranium is an element, the identification, separation and estimation of which are relatively easy.

Nevertheless, there are two circumstances which, by making it imperative that the methods be carefully selected, account for the considerable amount of analytical research work which developed in the course of the last few years on that subject, of which it can be assumed that only a fraction become the subject of technical papers.

These circumstances are: (*a*) the current demand for uranium; and (*b*) the high degree of purity required for the metal in its application in nuclear reactors.

This means that extremely sensitive methods must be developed (for instance: in order to determine the uranium content of very low grade ores and processing residues, the estimation of impurities in the oxide and in the metal, etc.). Furthermore, while remaining, in each case, within the limits of the precision required, the methods used must be such as to be carried out simply and speedily. Let it be stated that speed is the quality most sought, since it makes it possible to reduce the labor costs of the analytical control, which costs are still too high in view of the closeness and frequency of the control operations needed.

Allowing for these peculiar aspects of the problem, the Analytical Chemistry section of the "Comissão de Estudos de Energia Nuclear", in close cooperation with the "Junta de Energia Nuclear", began its study in the belief that it would be useless at the present time to look for new methods, and that one should simply select among those known, on the basis of the information supplied by the bibliographies, or transmitted by similar foreign organizations, thereafter to be confirmed by our own experience.

Some findings of this work in its present status are reported in this paper. It is concerned particularly with methods of estimating uranium in the ores mined on the Portuguese territory,† their concentrates and process tailings.

The need for operational speed and simplicity makes the classical gravimetric methods unsatisfactory. One of these methods is being used less and less as a standard method for U_3O_8 minerals of high or average U_3O_8 concentration, and we shall not consider separation methods such as mercury cathode electrolysis, extraction with solvents of cupferron complexes, etc.

The use of ion-exchange resins requiring much time and large elution volumes, and the application of certain physical non-automatic methods are to be thought of only in special cases.

We were, however, partially successful in our attempts to separate iron, aluminum, and phosphate by the cationic resins with elution by ammonium or sodium carbonate: the operation is somewhat lengthy, and although it is possible to avoid a release of CO_2, recovery of the uranium is often incomplete.

For the estimation of trace quantities, the elegant methods known as "activation" are inaccessible to us because we do not have a nuclear reactor or any other source of intense neutron fluxes.

Our experience with the other methods led us to select among the following: chemical attack, preceded or not by ustulation, is made with aqua regia followed by evaporation to dryness, dissolving once or twice in a suitable acid according to the purpose of the analysis and the contents of the sample. The other variable, namely the size of the sample, generally falls somewhere between 0.5 and 10 gm.

Accurate estimation is carried out as follows:

1. Following separation of iron (as well as of phosphate and aluminum): by oxidation-reduction volumetric analysis with Ce^{4+} or $Cr_2O_7^{=}$; we endeavored to replace Jones' column by an "internal" reduction process with $SnCl_2$ and Fe^{3+} as a catalyst, according to an American method.[1]

2. Without any previous separation: by use of a thiocyanate followed by spectrophotometric determination with $SnCl_2$ as to reduce the iron and copper as precipitant, using the current technique (very small amounts of uranium) or our "differential" method[2] (solutions containing 50 to 170 mg/liter of U_3O_8).

Polarography also is a good method, and one can avoid the separation of iron (and copper) by adopting

Original language: French.

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† Indication of the type of these minerals is made in a paper, P/968, published in Session 6B, Volume 6, of these Proceedings.

Table I. Methods

Separation	*Estimation*	*Special purpose*
Solvent extraction	Redox	Reference methods
Alkaline carbonate	Redox	
Alkaline carbonate	Colorimetry (H_2O_2)	Prospection
Chromatography (paper)	Polarography	Prospection
Chromatography (paper)	Fluorimetry	Prospection
None	Radiometry	Prospection
None	Polarography	Routine
None	Spectrophotometry (SCN)	Routine

the technique followed by the C.E.A.[3] or the more sensitive method of Legge.[4]

For geochemistry and health control, i.e., for the estimation of vanishingly small amounts, fluorimetry or spectrometry must be used.

We have not yet done any precision fluorimetry, but our method already has given the order of magnitude of the U content of some materials.

For the current needs of prospecting, in addition to the radiometric method which is the most useful, a rapid technique of measurement using hydrogen peroxide is in order, the measurements being made using a portable colorimeter equipped with filters.

As regards separation on a macro-analytical scale, we adopt the classical procedure, using ammonium carbonate or extraction of uranyl nitrate by an organic solvent; we do concede, however, that chromatography in a cellulose column with elution by ether or ethyl acetate also is a good method.

For low concentrations, the extraction of the nitrate is still to be recommended, but, in this case (and particularly for micro-quantities), the method of choice is paper chromatography. The duration of the elution may, in the end, be greatly reduced by making many simultaneous separations with very simple and cheap equipment. A rectangle of the paper strip which carries the separated uranium is incinerated and can be used for polarographic[5] or fluorimetric estimation.

For working under "standard" conditions and with a little training, this development is unnecessary, but this operation can be carried out without difficulty for the final measurement if the reagent is organic. For instance, an alcoholic solution of acid carmine gives good results if it is afterwards exposed to ammonia vapor. We even studied a colorimetric method of measurement using this reagent, which unfortunately is too sensitive to pH variations, and not very selective. Only the color with uranyl (green) is specific, but many other ions also give intense colors.

We feel that methods mentioned are adequate as regards U measurement. We have reason to expect, in a future which may not be immediate, some problems to be raised by the urgency of systematically making a great many analyses. These problems, however, are already in hand in those countries which are already advanced in the utilization of nuclear energy.

The problem will probably be solved by an examination of the statistical aspect and, for analytical chemists, by the elaboration of totally automatic physical methods. Among these, coulometry, which is still in its beginning, may have an important part to play, since it makes it possible to combine conventional titrimetry with modern electro-analysis, and with an obvious simplification.

Today, the selection of analytical methods is often confusing, not for a lack of references, but, rather, due to the over-abundance of papers, the results of which often disagree.

It is quite understandable and actually useful that each laboratory, in view of the unlimited potentialities of recently discovered means for chemical analysis, should try to find new methods different from those used by others. Often, however, this causes a real waste of time and labor.

In the case under study, it might be possible to direct this research on an international plane. This obviously would require a certain discipline, not to be imposed, but accepted, by those who might wish such discipline.

In this sense, it would be desirable for an Analytical Chemistry Commission, which might be a subsection of the U.I.C.P.A., to be directing a systematic research in the methods of analysis concerned with the use of nuclear energy for peaceful uses, thus functioning as an information and coordination center.

Thus, one would avoid a great many trials and error and useless multiplications of research and selection work.

The appended table shows the results of our selection of analytical methods, which are quantitative for uranium.

Of course, we are dealing with determinations of the element in the minerals of Continental Portugal: pitchblende, autunite, torbernite, without any thorium or rare earths.

Chemical attack and separation of uranium in the minerals of our East African territory (Moçambique): davidite, samarskite, euxenite, etc., are naturally different and often difficult. The analysis of the davidite of Tete (Mavusi) has been the object of earlier papers.[6] This mineral luckily contains only traces of Nb and Ta. However, other complex minerals which we have examined contained considerable amounts of these minerals. The estimation of uranium alone is often quite simple, but a complete analysis is one of the most complex problems in chemical analysis.

Even in the absence of phosphate, the separations are nearly always incomplete and purification of the precipitates at times difficult. We must note the difficulty in the estimation of thorium in those complex minerals. At the Center of Physics of the Commission of Nuclear Energy Study, the study of

the possibility of radiometric estimation[7] of U and Th in those minerals is being continued.

Until now we have made a revision of the polarographic methods of estimation of some elements of interest for the applications of nuclear energy[8] and, at the Analytical Chemistry Laboratory, we elected to use a technique of estimation of Be in beryl. The study of the analysis of the tantalocolombites goes on.

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Determination of Small Quantities of Uranium in Ores

By P. N. Paley, USSR

At the Academy of Sciences of the USSR the development of methods for the determination of small amounts of uranium in ores and other materials has passed through the same stages as abroad. In the beginning the classical methods of uranium determination and separation from other elements were used, then they were improved and later they were partly or completely replaced by more perfected methods.

In this report only the chemical methods are described, the development of physical and physicochemical methods of uranium analysis is given in a special one.

COLORIMETRIC METHODS OF URANIUM DETERMINATION

The reaction of uranium with hydrogen peroxide (peruranate formation) in alkaline media, in spite of low sensitivity was investigated in detail and for some years was widely used in the USSR for the analysis of low-grade ores, mainly because of the simple treatment required for the ore decomposition products with sodium carbonate to isolate uranium and to separate it from most of the associated elements (Zvenigorodskaja). Because of unavoidable complications in the methods of purification, which were necessary for the separation of some elements interfering with this reaction, for instance, copper, vanadium, molybdenum and others, it was almost completely substituted by other reactions.

The reaction of uranium with ferrocyanide is more sensitive but the colloidal solutions of the compound formed obeys Beer's law only under specific conditions.[1] Sinjakova and Klassova have stated that at a concentration of ferrocyanide and nitric acid of 0.02*M* and 0.05*M* respectively, the absorbance measured 15 minutes after addition of the reagents was proportional to the concentration of uranium over the concentration range 10–100 γ per 25 ml (Fig. 1). Measurements were made on a universal photometer, using a green filter (496 mμ). The presence of iron in amount less than 10% and vanadium 5% (of uranium content) did not interfere. The error was $\pm$ 3%. This method is used for industrial control, but its application to ore analysis is limited.

Belaja has investigated the reaction of uranium with *l*-ascorbic acid, which forms an unstable complex with uranium. Maximal coloration is produced only by using a large excess of reagent; when the absorption of a solution containing 15 γ U/ml is measured on a universal photometer using a violet filter (436 mμ), 0.4 gm of ascorbic acid is required (Fig. 2). In the presence of alkali carbonates the colour is stable for 24 hours or more. The sensitivity of this reaction is 5 γ U/ml at a pH = 4.4–4.5. The pH of the solutions is adjusted with the aid of *m*-dinitrophenol, the colour of which disappears at pH 4.5. To apply this reaction to ore analysis, a preliminary treatment with sodium carbonate is required. The remainder of the traces of iron, aluminium, titanium and manganese in the solution does not interfere. The influence of copper is eliminated by addition of sodium thiosulphate.

The reaction of uranium with sulosalicylic acid was investigated by Sinjakova and Klassova; this acid forms a coloured compound, the solutions of which obey Beer's law (Fig. 3) for uranium concentrations up to 0.250 mg per 25 ml, when measured using a blue filter (465 mμ). The optimal pH value of 4.4 (Fig. 4) is adjusted with "urotropin". A most intensive coloration is attained after 15 minutes and does not change for 60 minutes. (See Figs. 1 and 2.) Molybdenum, manganese and calcium in amounts not exceeding 20-fold that of uranium do not interfere. Vanadium produces a maximum absorbance at 500 mμ and in amounts less than 0.1 mg does not cause a notable error. Iron and copper must be absent. The sensitivity of this reaction is less than that with ferrocyanide.

Kazakov has isolated two compounds formed by sodium diethyldithiocarbamate with uranium: $UO_2(S_2NC_5H_{10})_2$ — yellow-orange, existing at a pH range of 2.5–7.0, and red $UO_2(S_2NC_5H_{10})_2 \cdot NaS_2NC_5H_{10}$ formed at a pH higher than 7.0.

The absorbance of aqueous solutions of the former at 320 mμ is 75% greater than that of the latter. Sinjakova and Klassova stated that in the pH range 6.6–6.8 and using a green filter (496 mμ) Beer's law is obeyed (Figs. 5 and 6) in the concentration range 0.01–0.5 mg U per 25 ml. Readings should be made 20 minutes after development of the colour and at a temperature of 15–20°. This reaction permits the determination of as little as 2.5 γ of uranium in 10 ml, but careful separation of many impurities (Fe, Cu, Mn, Ti, V and so on) is required. The intensity of the uranyl diethyldithiocarbamate colour may be increased by extraction into organic solvents (chloro-

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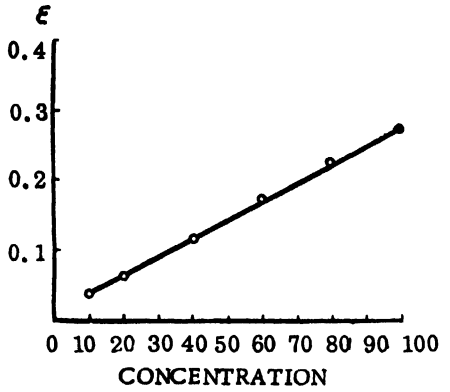

Figure 1. The dependence of the absorbance of ferrocyanide solutions on uranium concentration (γ/25 ml)

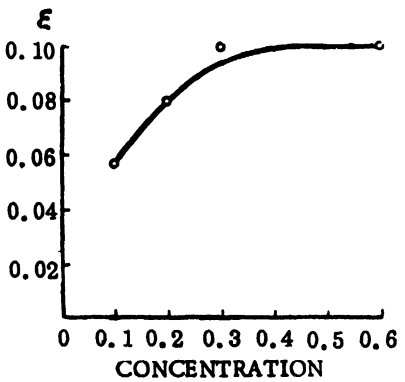

Figure 2. The dependence of the absorbance of uranyl solutions on ascorbic acid concentration (gm/50 ml)

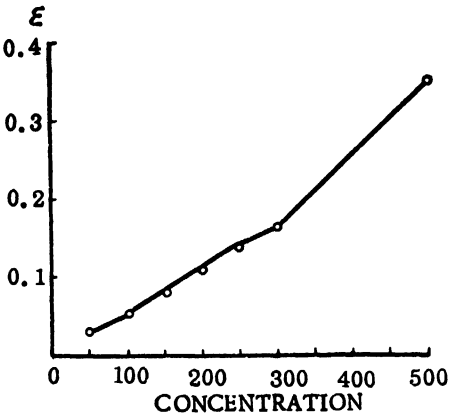

Figure 3. The dependence of the absorbance of uranium and sulphosalycilic acid solutions on uranium concentration (γ/25 ml)

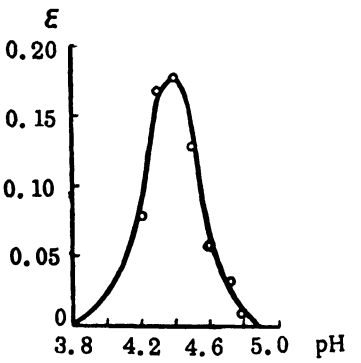

Figure 4. The dependence on pH of the absorbance of uranium and sulphosalycilic acid solution

form etc.). The absorbance of the chloroform solutions is nearly constant in the range 360–410 mμ. Therefore it is suitable to make measurements at 380 mμ. The molar absorption coefficient of the chloroform solution (α_{380}) is 4050. Beer's law is obeyed up to concentrations of 0.1 mg U/ml. The absorbance of the chloroform solution does not change for 6 hours while that of an ethyl acetate solution increases by 3.5–4% for 1 hour and then decreases. In aqueous solutions the absorbance decreases by 20% in 6 hours.

The absorbance at 380 mμ of iron, copper, nickel and cobalt compounds in organic solvents is high, therefore they should be removed (see below).

In aqueous solutions the reaction of uranium with thiocyanates has a lower sentivity, than other reactions, even than the reaction with hydrogen peroxide. The influence of many cations on the absorbance at 350 mμ in acetone-water solutions (60% acetone) was investigated. It was found that addition of a reducing reagent, such as stannous chloride does not noticeably influence iron and copper if the amounts of these elements do not exceed those of uranium. Titanium and vanadium in amounts equalling that of uranium cause increased results, whereas molybdenum decreases them. The reaction with thiocyanates is successfully used for uranium ore analysis only in combination with purification by extraction.

Soviet investigators have suggested new reagents for uranium determinations, the most sensitive of all known. For instance, the reagent "arsenazo" (phenyl-2-arsonic-acid-<1-azo-2>-1,8 dioxynaphthalene-3,6-disulphonic acid) suggested by Kuznetsov is of high sensibility (at dilutions up to $1:10^7$); it produces a blue coloration with uranyl-ions in the pH range 4.5–6.0. Optimal pH is 4.5–4.9. The solution is neutralized by "urotropin", using congo-red paper as an indicator. Excess reagent should be avoided, since it produces a mixed violet colour, not specific for uranium. Copper, thorium, vanadium, aluminium, rare earths and some other elements form coloured compounds with "arsenazo."

The reagent "toron" (phenyl-2-arsonic acid-<1-azo-1>-2 oxynaphthalene-3,6-disulphonic acid), also suggested by Kuznetsov, produces in hydrochloric acid solutions an extremely sensitive colour reaction (rose colour) with quadrivalent uranium. Nikolayev and Sorokina reduced U(VI) to U(IV) with iodides and the free iodine was removed by bubbling nitrogen through the solution. This reagent permits the determination of as little as 10^{-8} gm of U/ml. The most suitable range of concentrations for colorimetric measurements is 1×10^{-7}–2×10^{-6} gm/fl. The following do not interfere: U(VI) in relation to U(IV) up to 1000:1; V(III)—up to 16:1; Cr(III)—6:1; Fe(III)—200:1; Th—10:1; Al, Fe(II), Zn, Ce

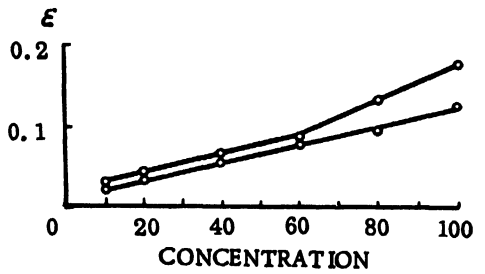

Figure 5. Dependence of the absorbance of sodium diethyldithiocarbamate solutions on the uranium concentration (γ/25 ml)

(III), La(III), Be, Ca do not interfere at all. $SO_4^=$, NO_3^-, F^-, phosphates, oxalates and organic substances do interfere and must be completely removed.

VOLUMETRIC METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF URANIUM

The investigations of Soviet scientists (Syrokomsky[8]) have shown that in sulphuric acid solutions the potential of the system V(V)/V(IV) increases sharply with increasing acid concentration and in 27N H_2SO_4 solution attains + 1.45 volt. On this basis a new field of redox volumetric analysis — vanadatometric analysis—was developed.

A standard solution of ammonium vanadate is prepared by dissolving a weighed quantity of the pure salt in 250 ml of sulphuric acid solution (1:1) and diluting it to 1 liter. For the determination of small quantities of uranium, the titre is checked by a standard solution of uranyl sulphate (prepared from pure metal or U_3O_8), previously reduced with cadmium or bismuth in a reductor. The use of phenylanthranilic acid, as an indicator, allows the titration to be carried out accurately in sulphuric acid solution (1:2) on as little as 0.1 mg of quadrivalent uranium (Alimarin). The quite distinct colour changes in a volume of 15–20 ml are observed even if making use of very diluted solutions of ammonium vanadate (up to 0.0004*N*) and 1–2 drops of the 0.2% indicator solution (Volkov).

Ammonium vanadate can be successfully used for determination of quadrivalent uranium in the presence of quadrivalent vanadium; it was shown that in the bismuth reductor, uranium and vanadium were reduced in 5*N* sulphuric acid medium only to the quadrivalent state (Paley, Skljarenko).

The potential of metal bismuth in sulphuric acid solutions, as measured by Gusev and ourselves, is equal to: in 0.5*M* H_2SO_4 = +0.218; in 1*M* = +0.208; in 2.5*M* = +0.180; in 5*M* = +0.166 volt vs normal hydrogen electrode, that means it decreases with increasing acidity. Since the potential of the system U(VI)/U(IV) increases under the same conditions, the reduction of uranium by bismuth occurs more rapidly in more acidic solution.

The oxidation of quadrivalent uranium by air is shown to be accelerated in light, especially in sunlight or ultraviolet light.

The catalytic effect of molybdenum and copper under these conditions is proved to be even greater. Thus, in 30 min in scattered daylight, solutions of 5 mg of quadrivalent uranium sulphate in 6*N* sulphuric acid were oxidized by 0.8% on illuminating with a quartz lamp LUM-1 by 32.2%. With decreasing sulphuric acid concentration (4, 2, 1*N*), the oxidation rate increases some tenfold. In the presence of hexavalent uranium the oxidation is accelerated; Thus at a ratio U(VI):U(IV) = 1:1, with air bubbling through the solution (10 mg U in 50 ml) for 3 hours, at a rate of 2 liters per hour, the oxidation was: in the dark—0.5%; in scattered daylight at a 3-meters distance from a window—11%; on the window-sill—33%; in the sunlight—60%.

The presence of divalent iron (1% of uranium) causes a delay in the oxidation. The presence even of a small quantity of molybdenum (0.1% of uranium) caused the oxidation of 5% of the uranium in the sunlight within 5 minutes without air blowing through the solution. Copper in quantities of 0.01% of uranium accelerates the oxidation twofold (Paley-Rengarten).

METHODS OF SEPARATION FROM ASSOCIATED ELEMENTS

The methods of separation of uranium from iron, calcium and many other elements by treatment with sodium carbonate solution was the most widely used for a long time. In the presence of large amounts of calcium, uranium is retained by the precipitate and thus calcium should be removed beforehand by means of precipitation with ammonium hydroxide. In this case copper, nickel and some molybdenum were also removed. The separation from vanadium was usually achieved by the precipitation of uranyl-ion as phosphate. For ores rich in vanadium reprecipitation of phosphate is required. Although these classic methods of separation allow complete analyses to be made both by colorimetric and volumetric methods, they are time and labour-consuming.

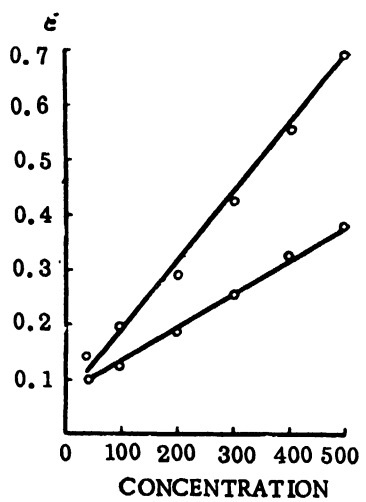

Figure 6. Dependence of the absorbance of sodium diethyldithiocarbomate solutions on the uranium concentration (γ/25 ml)

Later, these methods were considerably improved: precipitation by ammonium hydroxide was replaced by pyridine precipitation (Ostroumov) which reduces the uranium losses caused by the absorption of carbon dioxide from the air; the reduction of vanadium to the quadrivalent state by tartaric acid allowed uranium to be separated from large quantities of vanadium by a single phosphate precipitation; for ores rich in vanadium, instead of carbonate purification it was proposed to isolate uranium from acetic acid solutions as calcium uranovanadate, with an excess of the calcium salt and followed by subsequent precipitation of uranyl phosphate to separate it from vanadium (Nenadkevich).

In the presence of "trilon B" uranium(VI) may be precipitated by ammonium hydroxide, whilst the soluble complexes of iron, vanadium(IV), chromium, molybdenum, tungsten etc., described by Pribil,[5] remain in the solution. Vanadium(V) does not form a soluble complex with "trilon B", but is easily reduced to the quadrivalent state by heating. For small uranium contents (less than 0.5%) this method is unsuitable, since excess trilon B increases the solubility of ammonium diuranate, and the absorption of impurities by the precipitate calls for reprecipitation. The precipitate, after dissolving in 5*N* sulphuric acid, may be reduced in a bismuth or cadmium reductor and the uranium(IV) can be titrated with vanadate. For instance, for the standard ore No. 8, with a uranium content of 0.563%, it was found: 0.55% and 0.56% after reprecipitation, and 0.63% without reprecipitation (Paley, Poznyakov).

Among new methods developed in the USSR in recent years, are methods which are based on the ability of quadrivalent uranium to form compounds insoluble in mineral acids. This allows uranium to be separated from many impurities by a single precipitation. In some cases such precipitates can be directly used for volumetric determination.

Thus phosphates precipitate uranium(IV) from dilute solutions of hydrochloric or perchloric acids. Under these conditions the smallest quantities of uranium ($\sim 1\ \gamma$) may be quantitatively co-precipitated with thorium or zirconium phosphates, and thus be separated from iron, manganese, vanadium and most of the other elements (Volkov). The reduction of uranium to the quadrivalent state is produced with sodium hyposulphite or bivalent chromium (see below).

Uranium tetrafluoride is precipitated from uranium solutions, previously reduced with zinc and containing minimal amounts of mineral acids, by hydrofluoric acid; in this way zirconium and tantalum are completely removed. The precipitates are isolated by centrifugation, because they are difficult to filter.

The isolation of double fluorides, for instance $NaUF_5$, is more profitable because of their low solubility in strong acids (even in 1*N* sulphuric acid).

Under these conditions (1*N* H_2SO_4) the fluorides of molybdenum, titanium, nickel, cobalt, manganese, copper, iron(II) and even of trivalent vanadium do not precipitate. Aluminium precipitates completely as Na_3AlF_6. Iron(III) precipitates in part. The precipitate, after washing with a solution of hydrofluoric acid and sodium fluoride, may be titrated directly with vanadate in a sulphuric acid medium (1:2).

The reduction of uranium(VI) in the presence of fluorides can be made with bivalent iron, since the formation of stable complexes of FeF_6^{3-} and UF_5^- displaces the potentials of the systems UO_2^{2+}/U^{4+} and Fe^{3+}/Fe^{2+} in opposite directions (Table 1). In 3*M* HF, the real potential of the system Fe^{3+}/Fe^{2+} proved to be 220 mv more negative, ensuring the complete reduction of uranium.

Table 1. The "Real Potentials"[6] of the Systems Fe^{3+}/Fe^{2+}, UO_2^{2+}/U^{4+} and VO^{2+}/V^{3+} in 1N Sulphuric Acid at Different Concentrations of HF (vs Normal Hydrogen Electrode)

HF mol/l	Fe^{3+}/Fe^{2+}, *volt*	UO_2^{2+}/U^{4+}, *volt*	VO^{2+}/V^{3+}, *volt*
0.0	0.67	0.48	0.40
1.0	0.49	0.58	0.48
2.0	0.44	0.60	0.53
3.0	0.40	0.62	0.55
4.0	0.40	0.63	0.57

To determine the uranium in low-grade ores (1.0–0.00%) co-precipitation with carrier (calcium) is employed. The precipitate is treated with nitric acid and a little boric acid, uranium is brought into solution with sodium carbonate and determined by the peroxide method (Zvenigorodskaya, Rudina, Ryanitseva).

The separation of some contaminants (Fe, Ti, V, Ta, Nb, Zr, Sn, Sb, etc.) from $U^{(VI)}$ by cupferron precipitation from sulphuric acid solutions with subsequent reduction of uranium to the quadrivalent state and its reprecipitation with the same cupferron has been suggested by Holliday and Cunningham.[7]

However, the destruction of cupferron with H_2SO_4 + HNO_3 mixture, before reduction made this method time-consuming. For that reason a new, more simple variant was worked out, which was based upon the separation of copper, molybdenum, lead and bismuth with thiosulphate and the use of sodium hyposulphite as a reducing agent. The separation of Fe, V and other elements by cupferron is made in 10% H_2SO_4 medium, and the isolation of uranium(IV) in a 5% H_2SO_4 medium. This method requires 5 hours and gives results of high accuracy, if it is completed gravimetrically ($\pm 0.3\%$). But, if the content of uranium is less than 5%, the accuracy is lower and it is more advisable to use extraction methods (Elinson and Oleznyuk).

The other method consists in the following: after reducing uranium and separating it from some of the contaminants on a mercury cathode (anode is separated by a diaphragm) in a sulphuric acid

medium, quadrivalent uranium is quantitatively precipitated as the sulphate by addition of 2 volumes of 72% perchloric acid. The precipitate is easily filtered and, after washing with 47% perchloric acid, can be very accurately titrated with potassium permanganate. The method is applicable to amounts of U of 10 mg and more (Ponomarev, Dragomirova).

Extraction methods of separation of uranium are used from the very beginning, as the most effective for accurate analyses. They have been very much improved (Vinogradov).

As solvents for uranyl nitrate extraction besides ether, methyl-ethyl ketone (distribution coefficient ~ 25 at 60% NH_4NO_3 and 1*N* HNO_3) and an incombustible mixture of methyl-ethyl ketone with carbon tetrachloride (1:2) (Kusnetzov) and tributyl phosphate are used.

It was found, that anions such as F^-, SO_4^{2-}, VO_3^-, MoO_4^{2-}, PO_4^{3-} even in small quantities, interfere with the extraction of uranyl nitrate; this effect may be eliminated by the addition of aluminium or trivalent iron (up to 1–2*M*), suggested by Scott[8] as salting-out reagents. Small quantities of iron and aluminium (0.5–1.5 mg), which have passed into the organic layer, are removed for precise measurements by a second extraction from ammonium nitrate medium (Paley, Dobkina). Double extraction may be partly replaced by the re-extraction of iron and other elements in an apparatus (Fig. 7) in which ether passes first through the solution to be investigated, containing iron or aluminium nitrates, and then through the washing solution of ammonium nitrate (Michaylov).

The uranium may be very easily extracted with methyl-ethyl-ketone in the presence of ammonium thiocyanate. The coefficient of distribution between the ketone and the solution containing 60% NH_4NO_3 and 3% NH_4CNS, is 2000. Under these conditions iron is also extracted. Instead of methyl-ethyl-ketone, amylacetate, amyl alcohol and other oxygen-containing solvents may be used (Kuznetsov).

Uranium is extracted from tartaric and acetate buffer solutions (pH 3.7–7.0) by a 0.1*M* solution of 8-oxyquinoline in chloroform; uranium can be easily re-extracted from this solution by a 3% solution of ammonium carbonate, the complete separation of copper and other elements also occurring (Paley, Mirkina).

Extraction of uranium as the diethyldithiocarbamate can be applied to the separation from elements which are not precipitated with hydrogen sulphide. Among a number of proposed solvents chloroform is the most suitable, since extraction with light solvents in separating funnels lead to losses. For the chloroform extraction, adjusting the pH to the range of 6.6–6.8 is necessary. Uranium is extracted from the chloroform into the aqueous layer with ammonium carbonate, because of the decomposition of uranium diethyldithiocarbamate by the latter. By this means uranium is separated from iron, copper

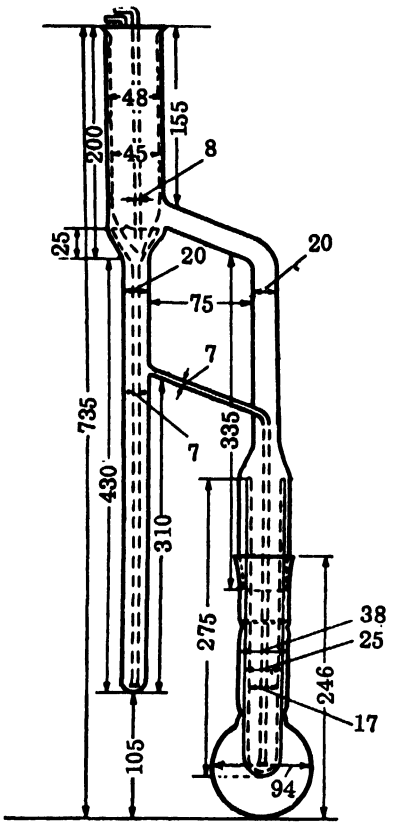

Figure 7. Extractor

and other elements remaining in the chloroform (Tsernichov and Dobkina). The number of elements extracted into chloroform, as diethyldithiocarbamates, may be greatly reduced by converting them into complex compounds with trilon B (see below).

In certain cases it is more convenient to extract not the uranium, but the impurities, which interfere with the volumetric estimation. A mixture amyl acetate with toluene (1:1) has been found (Kuznetsov) to extract completely vanadium(V) and iron (III) out of solutions containing 8.5 moles of sulphuric acid and 1.4 moles of hydrochloric acid per liter. For the vanadium(V), the coefficient of distribution is ~ 23, and for uranium(VI), 8000-fold less. To oxidize vanadium to V(V) potassium chlorate is added; W, Cr, and Sn are extracted simultaneously. The aqueous solution is evaporated to dryness and the residue is gently ignited. After dissolving it in sulphuric acid and reducing, U(IV) is titrated with vanadate.

NEW METHODS OF DETERMINATION OF URANIUM IN ORES

Phosphate Method

The principle of the method is the reduction of uranium(VI) with sodium hyposulphite, co-precipitation of uranium(IV) phosphate with thorium phosphate from acid solution, dissolution in sulphuric acid and titration with ammonium vanadate (Volkov). Phosphates were shown to precipitate quadrivalent uranium in moderately acid solutions $[H^+] = 0.35N$

as $U(HPO_4)_2 \cdot nH_2O$; the composition of the precipitate not depending upon the concentration of phosphate in the range from $1 \times 10^{-4}M$ to $1.4M$. The residual concentration of uranium (measured by α counting of U^{233}), at a constant concentration of hydrogen ions $[H^+] = 0.35M$, decreases with increasing phosphate concentration; at a phosphate concentration of $2.4 \times 10^{-2}M$, the residual concentration of uranium passes through a minimum at $2.4 \times 10^{-6}M$ and increases on further increasing the phosphate concentration.

The effect of acidity on the phosphate solubility is given in Table II (Moiseyev).

Since the solubility of the phosphates of most of the elements associated with uranium is many times higher in acid media than that of uranium, uranium(IV) may be separated from them by a single precipitation. Under these conditions co-precipitation of thorium, zirconium and some titanium do not interfere with the subsequent oxidometric determination of uranium.

For reduction of uranium to the quadrivalent state, either sodium hyposulphite ($Na_2S_2O_4$), already proposed by Kohlschutter and Rossi,[9] or "rongalite" $Na_2H_2S_2O_4 \cdot 2CH_2O \cdot 4H_2O$—formaldehydosulphoxilate of sodium) is used.

The reduction with "rongalite" is carried out on heating to 80–90° (Moiseyev). The quantity of hyposulphite, which is chiefly spent on reduction of uranium and iron, is 1 gm per 1 gm of sample.

On reduction with hyposulphite, free sulphur and sulphides of metals of the hydrogen sulphide group are precipitated; when the phosphate precipitate is dissolved in sulphuric acid, they remain on the filter.

The reduction and precipitation of uranium is suitable for use in hydrochloric or perchloric acids solutions; sulphuric acid retards the precipitation of uranium phosphate. Large amounts of sulphates cause incomplete precipitation of uranium phosphate. Nitric acid interferes with reduction.

In the presence of large amounts of fluorides, uranium phosphate does not precipitate. Even small amounts cause considerable losses. That is why it should be carefully removed after decomposition of ores with hydrofluoric acid.

Aluminium and chromium in large concentrations (greater than 0.2 gm per 100 ml) cause incomplete precipitation; in such cases the solution should be diluted.

Large quantities of lead are precipitated from cold solutions as white hyposulphite, which, while uranium phosphate is being dissolved in sulphuric acid, is decomposed with formation of sulphurous acid and thus gives high titration results. On heating, lead precipitates as the black sulphide, which is less soluble in sulphuric acid. In analysis of sulphide ores it is more suitable, before addition of the hyposulphite, to precipitate metals of the sulphide group with hydrogen sulphide or sodium thiosulphate on heating and to separate them.

In the most precise analyses the sulphide residue is ignited, dissolved in perchloric acid and the metals are removed with aid of a Hg-cathode. The solution, containing uranium retained by the sulphides, is added to the main solution.

In the analysis of low-grade ores or residues, it is necessary for complete isolation of uranium to add a co-precipitant—thorium or zirconium chlorides. The latter is less suitable, because of the slower coagulation of the precipitate and the difficult solubility in sulphuric acid.

Procedure (Volkov)

The acidic solution obtained after decomposition of an ore by a method suitable for its mineralogical composition, and removal of the insoluble residue, is neutralized with ammonium hydroxide with Metanil Yellow, as indicator (pH 2.3); 8 ml of hydrochloric acid (1:1) is added and the solution is diluted to 200 ml. 10 ml of a 10% solution of disodium phosphate; solid sodium hydrosulphite (1 gm per 1 gm of the sample, but no less than 0.5 gm); 4–5 ml of thorium chloride solution (containing 5 mg of Th per ml) and some filter paper pulp are added to the cold solution. The solution is then allowed to stand, stirred from time to time until complete coagulation of the precipitate and clearing of the solution takes place (about 40–60 minutes). The solution, with the precipitate, may be left overnight.

The solution is filtered by suction, using a thick filter "blue band". The precipitate on the filter, and the beaker with particles of the precipitate stuck to it, are washed with diluted hydrochloric acid (2 ml of concentrated HCl per liter) until complete removal of the products of hyposulphite decomposition.

The precipitate is dissolved on the filter with sulphuric acid (1:2). The filter and the beaker are washed with an acid solution of the same concentration. The solution (the volume of which is less than 30 ml) is collected in a conical flask, one drop of the indicator (0.2% phenylanthranilic acid solution in 0.2% solution of sodium carbonate) is added, and the solution is titrated immediately with a solution of ammonium vanadate of suitable concentration (from 0.01 to $0.0005N$).

Table II. The Solubility of Quadrivalent Uranium Phosphate at 20°C

pH	*4.1*	*1.8*	*1.3*	*0.7*	*0.45*	*0.3*	*1N HCl*
Solubility in moles/litre	2.1×10^{-7}	2.1×10^{-6}	4×10^{-6}	2.6×10^{-5}	6.4×10^{-5}	1.6×10^{-4}	6.1×10^{-4}

Table III. Ore Analysis by the Phosphate Method

Sample no.	*Content of U according the certificate, %*	*U, found with the phosphate method, %*
2	0.0802	0.80 ± 0.002
3	0.530	0.523 ± 0.003
5	0.218	0.219 ± 0.001
6	0.126	0.123 ± 0.002
7	0.059	0.061 ± 0.002
9	0.070	0.069 ± 0.001
10	0.108	0.107 ± 0.001

For low-grade materials (less than 0.01% of U), where larger samples (up to 5 gm) are required, complete washing of the phosphate and sulphur precipitates becomes difficult. In these cases a double precipitation is recommended. The once-washed precipitate is dissolved in hydrochloric acid (1:2); the filter is washed with the same acid. The solution is neutralized with ammonium hydroxide; acidified with 6 ml of hydrochloric acid solution (1:1) and diluted to 200 ml. Precipitation is repeated with reduced quantities of reagents added (5 ml Na_2HPO_4; 0.2 gm $Na_2S_2O_2$; 2 ml $ThCl_2$). The determination is carried out as described above.

In Table III the results of determinations of uranium in standard ore samples made with the phosphate method (average of 10 parallel determinations) are given.

For poorer materials the volumetric determination is replaced by a colorimetric ore (Ponomarev). In this case the phosphate precipitate is dissolved in a minimum quantity of 15% sulphuric acid. One ml of trivalent iron solution (0.1 mg of Fe per ml) is added and the solution is neutralized with sodium carbonate until faintly acid. After adding 0.5 ml of a 0.5% solution of α-α'-dipyridyl and stirring, 5 ml of of a 5% solution of borax is added. The solution is diluted to the correct volume and after half an hour the colour of the bivalent iron compound with dipyridyl is measured with a photometer. The results of the determination of uranium by this method are given in Table IV.

The other variant of the phosphate method is based on the reduction of uranium with bivalent chromium. The presence of large amounts of trivalent iron results in a high concentration of trivalent chromium and the precipitation of uranium is retarded. To avoid this, chromium is converted into a complex compound with thiocyanide or the consumption of bivalent chromium is decreased by previous reduction of trivalent iron with ascorbic acid.

Table IV. Ore Analysis by the Phosphate (Colorimetric) Method

Sample no.	*U, found %*		
	Vanadate titration	*Colorimetric method*	*The weight of sample for the colorimetric determination*
1	0.084	0.084 ± 0.002	0.1
11	0.049	0.049 ± 0.002	0.2
13	0.012	0.013 ± 0.001	0.3
14	0.0092	0.0092 ± 0.003	1.0

Procedure (Tsernichov, Lukhyanov)

To the clear solution (200 ml), containing 3 ml of conc. hydrochloric acid, the following are added in succession: 10–15 ml of 10% solution of $Na_2HPO_4 \cdot 12H_2O$; 0.5–15 gm of solid ammonium thiocyanate taking 2.5 gm of the latter per 0.1 gm of iron, 0.5*N* solution of chromous chloride till disappearance of the red coloration of the solution with iron thiocyanate and then an excess of 3 ml; 4–5 ml of the thorium chloride solution, containing 5 mg of salt per ml and finally some filter paper pulp.

The subsequent operations are the same as in the method already described.

The results of uranium determinations with this method are given in Table V.

For the determination of normal concentrations of uranium in rocks ($n \times 10^{-4}$%), zirconium is used instead of thorium, as co-precipitant. The washed and ignited precipitate is fused with sodium fluoride and the uranium is determined by the fluorescent method (Volkov, Razzhivina).

Diethyldithiocarbamate-Trilon Method

The principle of the method is based on the conversion of the most strongly associated elements into soluble complex compounds with trilon B, extraction of uranium diethyldithiocarbamate out of a neutral solution into chloroform, the re-extraction of uranium into an aqueous solution of ammonium carbonate. The determination of uranium is completed using microvanadatometric, colorimetric (making use of diethyldithiocarbamate) and fluorescent methods (Paley, Udaltsova).

Among the elements which react with diethyldithiocarbamate in neutral media and which can be extracted in its presence with chloroform, very many form much more stable complex with trilon B, namely iron, nickel, cobalt, indium, gallium, zinc, lead, vanadium, columbium and tin; in the presence of trilon B they are not extracted with chloroform. Only Be, Ti, Sb and to some extent Mn do not react with trilon B and may be precipitated on neutralization. Uranium, in the presence of trilon B, is precipitated only at pH 8.5; this indicates the

Table V. Ore Analysis by Chromo-Phosphate Method

Sample no.	*U content according to certificate, %*	*U, found with chromo-phosphate variant*
9	0.070	0.071 ± 0.002
7	0.059	0.059 ± 0.002
4	0.072	0.070 ± 0.001
15	0.237	0.239 ± 0.001
12	0.042	0.041 ± 0.002

formation of an unstable complex. Thus, acid solutions obtained after the dissolution of ores, may be neutralized in the presence of trilon B to the pH range of 6.6–7.0 without setting down large precipitates.

Besides uranium and copper, silver, bismuth, mercury, thallium, arsenic, selenium and tellurium are extracted from these solutions with chloroform as the diethyldithiocarbamates (Bode[10]).

On washing the chloroform extracts with ammonium carbonate, uranyldiethyldithiocarbamate is decomposed and uranium passes into the aqueous layer, the other elements remaining in the chloroform (Tsernichov, Dobkina).

Other solvents, such as diethyl ether, amylacetate, and isoamyl alcohol, may be used for extraction.

Procedure (Udaltsova)

To the clear solution (50 ml), obtained after dissolution of an ore and neutralisation with ammonium hydroxide till slight turbidity (pH not higher than 2.5–3), solid trilon B is added in quantities of 5–8 gm per gm of a sample. (For ores rich in iron the quantity of trilon should be increased to 10 gm per gm of sample.) The solution is adjusted with ammonium hydroxide to the pH range 6.6–7.0 with litmus paper and transferred into a separating funnel; 5 ml of 2% aqueous solution of sodium diethyldithiocarbamate is added and the solution is shaken. The diethyldithiocarbamates formed are extracted into chloroform taking 5–7 ml in each portion; the extraction is continued until the chloroform layer is colourless. Usually 5–7 extractions are required.

The chloroform extracts are gathered into a second separating funnel, 2–3 ml of a 2% solution of ammonium hydroxide and 5–6 drops of a saturated solution of ammonium carbonate are added and the solution is vigorously shaken for 2–3 minutes. The aqueous layer, containing uranium, is transferred into a quartz or porcelain dish, evaporated to dryness and the residue ignited at 500–600° for 30 minutes. The residue is then dissolved in nitric acid, converted to the sulphate and the uranium is determined by the volumetric method.

For polarographic, colorimetric or fluorescence analysis conversion into sulphates is not necessary.

The results of the determination of uranium by this method (including vanadatometric methods) are given in Table VI.

Table VI. Analysis of Uranium Ores by the Trilon B Method

Sample no.	*U according to certificate, %*	*U found, %*
7	0.059	0.059 ± 0.003
5	0.218	0.219 ± 0.003
6	0.126	0.125 ± 0.002
16	0.328	0.327 ± 0.001
9	0.070	0.069 ± 0.004

The Thiocyanate Method

The principle of the method is: separation of uranium from impurities by extraction of the uranyl salt into methyl-ethyl ketone, with subsequent spectrophotometric determination of uranium thiocyanate in a methylethylketone-acetone mixture (Sinyakova, Novikov).

The spectrophotometric determination of uranium as thiocyanate in aqueous-acetone solutions was investigated earlier; in this medium the interference of iron, copper, sulphates and fluorides is less than in aqueous medium, but their influence still affects the results of the determinations even when they are present in less quantities than usually found in ores; thus preliminary separation is required.

For extraction methylethylketone is used with NH_4NO_3 as a salting-out agent. From a 10 ml solution, uranyl nitrate is extracted by two portions of methylethylketone of 2.5 ml each. On separating the organic layer, 6 ml of acetone are added to it, saturated with NH_4CNS and several milligrams of solid ascorbic acid, to reduce traces of Fe^{3+}. The solution is adjusted with methylethylketone to 10 ml. The absorbance of the solution at 375 and 400 mμ is measured using 10 mm cells. A mixture of methylethylketone with 6 ml of acetone, saturated with NH_4CNS and containing ascorbic acid, is used as a blank. As can be seen from Fig. 8 Beer's law is followed in the concentration range 0.01–0.15 mg U/ml.

The absorbance of solutions containing different amounts of ammonium thiocyanate was investigated and it was found that with decreasing ammonium thiocyanate concentration, the absorbance decreased to some extent (Fig. 9). Thus, it is advisable to use saturated solutions of thiocyanate.

The dependance of the absorbance on time for the wave length 400 mμ within 100 minutes is not notable; for 350 and 375 mμ the absorbance within 10 to 40 minutes is constant, and then gradually increases. Therefore it is advisable to make readings 30 minutes after the addition of thiocyanate.

Small amounts of impurities which may be extracted together with uranium, may influence the absorption. By special investigations it was found out that iron(III) is extracted in considerable quantity, but the addition of ascorbic acid completely eliminates its influence, even at a ratio U:Fe of 1:40, in aqueous solution before extraction. The same holds for copper and cobalt at a ratio 1:100. Vanadium, titanium and bismuth are extracted to some extent and do increase the absorbance value while molybdenum decreases it.

To eliminate the influence of molybdenum, lactic acid is used. One ml of 40% lactic acid per 10 ml of solution (saturated with NH_4NO_3) completely retains 5 mg of molybdenum in the aqueous layer and does not interfere with the extraction and determination of 0.5 mg of uranium.

The extraction of vanadium with methylethylketone may be eliminated by complexing of vanadate

Table VII. Ore Analysis with Thiocyanate

Sample no.	Content of U found with ether method, %	U found with thiocyanate method		Variant no.	Content of ore
		375 mμ	400 mμ		
10	0.108	0.105	1.108	3	Cu 0.01%; Fe 5%; Ti 0.3 %; Mo, V-nil
21	0.87	0.91	0.87	3	Cu 0.05%; Fe 10% Ti 1%; Mo, V-nil
19	0.288	0.285	0.285	3	
23	0.325	0.325	0.330	3	
26	0.080	0.090	0.090	3	V = 0.8%
24	0.270	0.270	0.270	4	

by zirconium salts. But the simultaneous use of zirconium and lactic acid is impossible because of precipitate formation.

Procedure

The thiocyanate method may be used in a number of ways in determining ores.

Method 1 is used if molybdenum, vanadium, titanium and bismuth are absent and copper, iron, cobalt (and other ions, not reacting with thiocyanate) are present. The method consists of the extraction of uranyl nitrate into methylethylketone from the solution saturated with NH_4NO_3, with subsequent formation of the uranium thiocyanate complex in the ketone layer and measurement of the absorbance of this solution after adding ascorbic acid. The analysis takes 30 minutes. The accuracy is 1–2% relative.

Method 2 is applicable in the presence of molybdenum and the impurities indicated for the first variant and differs from the first variant only by the addition of 0.5 ml of 40% lactic acid, before extraction.

Method 3 is applicable in the presence of the same impurities (excepting molybdenum) and it differs from the first by the addition of zirconium nitrate (10 mg Zr) before extraction.

Method 4 is used in the presence of vanadium, molybdenum, titanium, bismuth, iron, copper and cobalt and is based on the double extraction of uranium into methylethylketone. After the first extraction in the presence of lactic acid, uranium is re-extracted 3 times into 2% ammonium carbonate solution. The solution is evaporated to dryness. The residue is ignited in a muffle furnace and dissolved in nitric acid.

On saturating the solution with ammonium nitrate and adding zirconium nitrate, uranium can be extracted with ketone. After addition of NH_4CNS, the absorbance of the acetone solution is measured. Ascorbic acid is not required in this method. The analysis takes 3–4 hours. Accuracy is 2% relative.

The data obtained by the thiocyanate and standard ether methods are given in Table VIII (average of 10–12 determinations).

The method with thiocyanate may be used in industrial control, as an express-method.

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The Physical Method of Determining the Content of Uranium, Radium and Thorium in Radioactive Ores

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The main problem in exploring, prospecting for, and milling radioactive minerals is to determine the uranium, radium and thorium content in ores and rocks. Several physical, chemical and radiochemical methods are used for this purpose.

Modern physical methods for determining the content of radioactive matter in ores are based on registration of alpha, beta and gamma radiation.

Although physical methods, unlike chemical and radiochemical (radiometric) methods, are highly efficient and cheap, they cannot be substituted for the latter. The reason for this is that existing physical methods are capable of determining only the uranium content;[1,2,3] they are not able to determine the radium and thorium content except in a few specific cases.

The authors of this paper were confronted with the problem of developing a general physical method capable of determining with sufficient accuracy the uranium, radium and thorium content in radioactive ores. It should be noted that this paper does not concern itself with prospects of using specific physical methods such as the method of determining the uranium content in rocks from fission products, the method of determining the thorium content from the range of alpha particles, etc.

This paper deals only with one problem, the problem of developing a general physical method for determining the uranium, radium and thorium content in radioactive ores and rocks based on registering gamma and beta radiation from these rocks.

THE FUNDAMENTAL PRINCIPLES OF A PHYSICAL METHOD FOR DETERMINING SIMULTANEOUSLY THE URANIUM, RADIUM AND THORIUM CONTENT IN RADIOACTIVE ORES

Description of the Method

The method of determining simultaneously the uranium, radium and thorium content in ores and rocks consists of the following: the ore, ground into a powder, is placed in a cylindrical aluminum hermetically sealed container of special design. This container is set in the counting chamber of an apparatus that is to be used for simultaneously measuring the intensity of gamma and beta radiation emitted from the radioactive ore under study.

Original language: Russian.

The intensity of the total gamma radiation and the intensity of the hard gamma radiation having an energy greater than stipulated, are measured.

In the second measurement of gamma radiation intensity, energy cut-off is introduced. In this measurement the gamma radiation from the decay products of thorium are sharply accentuated because of the existence in their gamma ray spectrum of an intense line with an energy of 2.62 Mev.

From these two measurements the content in the ore of thorium and radium (or more correctly, of the decay products of radon) is determined.

Measurement of the beta radiation and the total gamma radiation intensity allows one to determine the uranium content in the ore.

In the apparatus that was developed, measurements of the gamma radiation intensity as well as measurements with energy discrimination are performed by means of Geiger-Mueller counters.

For registering gamma radiation, the apparatus contains two concentric rings of glass type Geiger-Mueller counters connected in parallel. The container with sample is placed in the inner space of this ring-shaped counter.

Energy discrimination of the gamma quanta is accomplished by means of a coincidence circuit. These pulses are sent out from both rings of counters. Registered coincidence corresponds to those cases when the secondary electrons, created by gamma quanta in the walls of the counter, pass through the counters in both rings.

The energy discrimination level of gamma quanta in such a counter, as will be shown below, is determined by the wall thickness of the adjacent counters.

Intensity measurement of beta radiation from the sample is performed by means of a thin walled Geiger-Mueller counter located within the sample container and set along the axis of the container in such a manner that the body angle of beta radiation registered is close to 4π.

Choice of Method of Counting the Gamma Radiation

It should be noted that the use of Geiger-Mueller counters in the apparatus as detectors of gamma radiation, at first glance, seems unjustifiable considering that they are not very efficient in registering gamma radiation.

In fact, scintillation counters are widely used for registering gamma radiation in current experimental studies.

The use of scintillation counters allows one to construct an apparatus in which highly efficient detection of the gamma radiation is coupled with a simple system of energy discrimination of gamma quanta.

These features of scintillation apparatus definitely correspond to the character of the problem being solved. Therefore, in principle, it seems quite expedient to use scintillation counters in apparatus determining uranium, radium and thorium content in radioactive ores.[3]

However, in spite of these advantages of scintillation counters, it is not always of advantage to use them in practice because the apparatus using Geiger-Mueller counters as detectors are simpler and more reliable than corresponding types of scintillation apparatus, the higher efficiency of which are not always necessary.

As was mentioned above, the uranium content of an ore is determined from intensity measurements of the gamma and beta activity in the sample. Therefore, the accuracy with which the uranium content in the ore is determined will depend upon the accuracy of the intensity measurement of these radiations. It is evident that those measurements having the larger permanent errors will limit the accuracy.

It turns out that when simultaneously measuring the intensity of gamma and beta radiation emitted from a sample of radioactive ore, the limiting radiation, from the point of view of accuracy of measurement, is the beta radiation. Therefore, any increase in the efficiency of registering gamma radiation which at the same time does not alter the registration of beta radiation will be of no value, because the accuracy of determining the uranium content in the ores under consideration is not increased. Consequently, the use of the less reliable and more complicated scintillation apparatus for these purposes, at the present, has no meaning since the most simple solution to the problem can be found by using instruments equipped with Geiger-Mueller counters.

In order to obtain the required results when using Geiger-Mueller counters as detectors of gamma radiation, it is necessary to take into account the specific physical conditions of measurement. A description of the measures taken is given below. Unsuccessful attempts using Geiger-Mueller counters and coincidence circuits in the analysis of uranium-thorium ores[4] emphasize the importance of introducing these measures. These attempts did not give a practicable method for the determinations that interest us.

Elimination of the Influence of Chemical Composition of the Rock on the Results of Measuring the Uranium, Radium and Thorium Content

In order to obtain definite results in determining the content of radioactive matter in rocks and radioactive ores, measurements should not be influenced by the chemical composition of the rock.

It is known that for all practical purposes beta radiation does not depend upon the chemical composition of the radiating substance. It is important in beta measurements to create conditions, whereby the registered beta radiation is emitted from a layer of substance that is known to be "thick"; that is, the layer should be thick enough so that a further increase of its width would not influence the intensity of beta radiation. Under these conditions the intensity of beta radiation will depend upon the content of radioactive matter in the ore.

It is necessary that intensity measurements of gamma radiation should be independent of the chemical composition of the radioactive ore. They should be proportional only to the content of radioactive matter in the ore. This is achieved by filtering the gamma radiation of the sample with a layer of lead having a thickness of 1 to 1.5 mm. Such a filter blocks out the soft components of the gamma radiation spectrum and leaves only hard gamma quanta. Absorption of the latter is practically independent of the chemical composition of the emitting substance.

Moreover, in gamma measurement, it becomes quite necessary to establish a condition whereby the absorption of gamma radiation in the emitting substance is negligibly small. This condition is fulfilled by using a lead filter and choosing appropriate dimensions for the container in which the sample is placed.

Determination of the Radium and Thorium Content

As was mentioned above, the thorium and radium content in the ore (strictly speaking, not radium content, but content of decay products of radon) can be determined by performing two measurements of gamma radiation intensity, namely, a measurement of the whole gamma radiation intensity N^{Γ} and a measurement of the hard gamma radiation intensity N^{γ}. The content of unknown radioactive elements can then be calculated from the following equations:

$$N^{\Gamma} = (aR_{Ra} + bR_{Th})P$$

$$N^{\gamma} = (a\chi_{Ra} R_{Ra} + b\chi_{Th} R_{Th}) P$$

$$R_{Ra} = \frac{N^{\Gamma}\chi_{Th} - N^{\gamma}}{a(\chi_{Th} - \chi_{Ra})P} \quad (1)$$

$$R_{Th} = \frac{N^{\gamma} - N^{\Gamma}\chi_{Ra}}{b(\chi_{Th} - \chi_{Ra})P} \quad (2)$$

where R_{Ra} is the content of decay products of radon in the ore, in per cent; R_{Th} is the content of thorium in the ore, in per cent; N^{Γ} is the counting rate of total gamma radiation recorded; N^{γ} is the counting rate of hard gamma radiation recorded; $\chi_{Th} = (N^{\gamma}/N^{\Gamma})_{Th}$ is a factor diminishing the counting rate for "thorium" gamma radiation; $\chi_{Ra} = (N^{\gamma}/N^{\Gamma})_{Ra}$ is a factor which corrects the counting

rate for gamma radiation from the decay products of radon, RaC and RaB; a and b are constants depending upon the parameters of the apparatus, test conditions and yields of gamma radiation from the thorium and uranium series; and P is the weight of the sample.

The emanation factor of the sample has to be specially measured in order to determine the radium content. After this, the data is used to calculate the content of the decay products of radon, which gives the radium content.

The emanation factor of the sample can be determined by the usual radon method. If for any reason it is undesirable to use the radon method, the emanation factor can be determined by using the apparatus described in this paper. In this case successive measurements of the beta radiation intensity of the sample are performed. The emanation factor is determined by the rate of increase of intensity of "beta activity."

In order to determine the emanation factor, measures are taken to eliminate the leakage of radon from the containers in which the samples are placed. Hermetically sealed containers are also necessary to eliminate thoron leakage, since it may somewhat alter results of the thorium determination (when calculating thorium content it is assumed that thorium is always in a state of equilibrium with its decay products).

It should be noted that precise determination of the radium content is necessary only in a few special cases where the genetics of mineral deposits or ore formation is being studied. The practical work of geological exploring parties or the mining of radioactive ore requires a precise determination of uranium and thorium content only. A precise determination of the radium content for these purposes is of no consequence. Approximate information regarding the radium concentration is quite sufficient. This information can be gained from a determination of the content of decay products of radon in which the emanation factor is neglected. Therefore, in future we will conditionally regard the determination of decay products of radon as being identically the same as the determination of radium itself.

Determination of Uranium Content

When determining the uranium content, certain difficulties in the method arise due to the existence in the uranium series of a comparatively intense beta emitter, RaE, which is not found in a state of equilibrium with the decay products of radon. It was shown that RaE in the test sample almost always was in equilibrium with radium; however, it might not be in equilibrium with the decay products of radon having a short life due to the phenomenon of emanation and to the comparatively large half life of RaD. As a result, when deriving an expression for the counting rate of beta radiation, it is necessary to isolate the part of the beta radiation due to RaE which should be introduced as an independent variable. Beta radiation from potassium should be also considered in the general expression for beta activity of the sample.

$$N^{\beta} = CR_{U} + AR_{Ra} + BR_{Th} + LR_{RaE} + MR_{K} \quad (3)$$

where C, A, B, L, M are constants characterizing the part of measured beta radiation from the corresponding radioactive components; and R_{U}, R_{Ra}, R_{Th}, R_{RaE}, R_{K} are values for the content of the corresponding radioactive components in the test sample of radioactive ore.

There are five independent variables in Equation 3. This expression may be simplified by taking into account the relationship between the emission factors of beta radiation from a thick layer of the components Ra and Th in Equation 3 and the emission factor of gamma radiation from the same components in Equations 1 and 2.

$$\frac{B}{A} = \frac{b}{a}(1 + \epsilon) \quad (4)$$

where $e \ll 1$. After substituting Equations 4, 1 and 2 in Equation 3 and simplifying we find

$$N^{\beta} = CR_{U} + \frac{A}{aP}N^{\Gamma} + A\frac{b}{a}\epsilon R_{Th} + LR_{RaE} + MR_{K} \quad (5)$$

The third term in Equation 5 is, as a rule, insignificant in the general balance and therefore can be neglected. As a result:

$$N^{\beta} = CR_{U} + \frac{A}{aP}N^{\Gamma} + R_{RaE}L + MR_{K} \quad (6)$$

The last term in Equation 6 shows that the part of beta radiation from potassium is also not extremely significant in the general balance of radiation. Beta radiation from potassium should be taken into account only when studying extremely low-grade radioactive ores. Consequently, for ordinary measurements the last term in Equation 6 can almost always be neglected. In this case:

$$N^{\beta} = CR_{U} + \frac{A}{aP}N^{\Gamma} + LR_{RaE}$$

Assuming the concentration of RaE always to be proportional to the radium content then the content of RaE can be expressed in terms of equivalent uranium content. As a result, we have:

$$N^{\beta} = CR_{U} + \frac{A}{aP}N^{\Gamma} + L\xi R_{U}$$

where ξ is the equilibrium factor of RaE with uranium.

Solving this equation for R_{U} we obtain:

$$R_{U} = \frac{N^{\beta} - \frac{A}{aP}N^{\Gamma}}{C\left(1 + \frac{L}{C}\xi\right)} \quad (7)$$

Equation 7 contains only one independent parameter which is the equilibrium factor of RaE, ξ.

Table I

Thickness of aluminum filter mm	Relative weakening of beta radiation intensity					
	Uranium ore in equilibrium	Uranium	Thorium	Radium without RaE	RaE	K
0.1	1.0	1.0	1.0	1.0	1.0	1.0
0.3	0.56	0.61	0.6	0.59	0.23	0.42
0.6	0.32	0.34	0.38	0.41	0.05	0.17
0.9	0.19	0.21	0.25	0.24	0.01	0.07

Under natural conditions this factor can vary within extremely wide limits. The numerical value for the ratio of the factors L/C, when directly registering beta radiation emitted from a thick layer, is close to 0.3. Therefore, Equation 7 is not as yet suitable for calculating the uranium content.

In order to determine precisely the uranium content, it is necessary to eliminate the effect of beta radiation from RaE on the beta measurements. For this purpose, it is possible to make use of the fact that the spectrum of beta radiation from RaE has a maximum energy considerably lower than the maximum energies in the spectra of the remaining components of the radioactive series.

Results of experiments for reducing the beta radiation by means of aluminum filters for five radioactive components buried in quartz sand are given in Table I. The thickness of the layer of activated sand was chosen so that beta particles were being emitted from the "thick" layer.

The data in Table I show that the beta radiation from RaE is reduced much more sharply with an increase in thickness of the aluminum filter than the beta radiation from the remaining radioactive components. With a filter thickness of 0.9 mm, the relative weakening of beta radiation intensity from RaE is twenty times greater than the relative weakening of beta radiation intensity from the decay products of uranium.

A further increase in thickness of the filter brings about a greater difference in the weakening of beta radiation. However, beta radiation from the main radioactive components is at the same time considerably reduced. Therefore, it is advisable to stop at a thickness of 0.9 mm for the aluminum filter, where beta radiation from uranium and RaC is not considerably weakened while radiation from RaE is almost totally absorbed.

Therefore, we have:

$$R_U = \frac{N^\beta - \frac{\chi^\beta_{Ra} A N^\Gamma}{aP}}{C\chi^\beta_U\left(1 + \frac{\chi^\beta_{RaE}}{\chi^\beta_U}\frac{L}{C}\xi\right)}$$

where χ^β_U is equal to 0.21 (see Table I) and χ^β_{Ra} is equal to 0.24 (see Table I).

In this case:*

$$\frac{\chi^\beta_{RaE} L}{\chi^\beta_U C} \approx 0.017$$

$$R_U = \frac{N^\beta - \frac{\chi^\beta_{Ra} A}{aP} N^\Gamma}{C\chi^\beta_U} \qquad (8)$$

Equation 8 does not contain unknown parameters. This expression is suitable for precise calculation of the uranium content on the basis of beta and gamma radiation even when the uranium and the radium contents deviate greatly from their equilibrium values. Only when equilibrium is violated by the presence of more than six times the required (equilibrium) amount of radium, do we observe a relative error in the determination of uranium content of more than 10%.

This accuracy of measurement is quite sufficient for the majority of practical purposes.

The Main Technical Requirements of the Apparatus

The principal physical prerequisites that serve as the basis of a method for simultaneously determining uranium, radium and thorium content in radioactive ores were considered above.

From this consideration, it is possible to formulate the requirements that the apparatus must fulfill.

1. The apparatus must simultaneously register gamma and beta radiation.
2. The apparatus must simultaneously register total gamma radiation as well as only hard gamma radiation having an energy higher than stipulated.
3. In order to eliminate the influence of the chemical composition of complex minerals on the measured results, gamma radiation should be filtered by a layer of matter having a large Z.
4. In order to eliminate the interference of beta activity, the RaE beta radiation from the sample should be filtered by a layer of aluminum having a thickness of 0.9 to 1.0 mm.
5. The sample container should have a hermetic seal, thereby eliminating leakage of emanations.

* In the following text $\chi_{Ra}{}^\beta A$ is designated by A and $\chi^\beta{}_U C$ is designated by C.

Table II

Zero background	Without anti-coincidence and lead	With anti-coincidence but without lead	Without anti-coincidence but with lead	With anti-coincidence and lead
Registration of total gamma radiation, cpm	2400	1900	520	210
Registration of coincident pulses, cpm	290	30	205	9.5
Registration of beta radiation, cpm	49	28	23	10

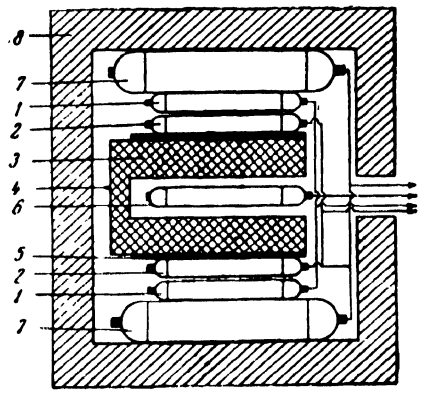

Figure 1. Cross section of case

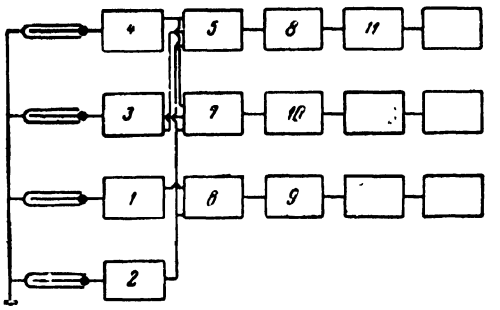

Figure 3. Block diagram of the apparatus. Blocks at right are mechanical registers (E.M.C.); blocks below block 11 are SC-64 scaling devices.

THE APPARATUS AND RESULTS OF TESTS

A Description of the Apparatus

The counting chamber of the apparatus is schematically shown in Fig. 1. A general view of the partially disassembled counting chamber and a view of the sample container are shown in Fig. 2.

Beta radiation is registered by a thin-walled Geiger-Mueller counter (see 6 in Fig. 1) placed in the center of the counting chamber in such a manner that while measuring, it is located in the central space of the container (see 4 in Fig. 1). The counter is mounted in a cylindrically shaped aluminum casing. The walls of this casing taken together with the walls of the inner space of the aluminum container form a filter that absorbs beta radiation RaE.

Gamma radiation is registered by means of two rings of glass counters of the BC-8 type connected in parallel (see 1 and 2 in Fig. 1). While the gamma radiation is being registered, the counting rate of the entire system of counters as well as the counting rate of coincident pulses is also being measured.

The use of coincident pulses for the energy discrimination of gamma radiation is a development of Bothe's method.[4] The discrimination system that was developed differs from the one in Bothe's method in that a ring group is used, containing 42 counters, which is equivalent to the 20 elementary nuclei in the latter method. The influence of chemical composition of the ore on gamma radiation is eliminated by a lead sheath (see 5 in Fig. 1).

The BC-8 type counters used in registering gamma radiation were treated with hydrofluoric acid in order to reduce the width of the glass walls in the counter; thus, the threshold of energy discrimination of secondary electrons is lowered.

The ring system of gamma radiation counters is surrounded by a tray of type BC-6 counters (see 7 in Fig. 1), connected for anti-coincidence with the remaining system of countries. This type of connection considerably reduces the background from cosmic radiations that have penetrated.

For reducing the background from soft cosmic and terrestrial radiations, the pick-up element in the apparatus is placed in a lead sheath having walls 50 mm in thickness (see 8 in Fig. 1).

The way in which the anti-coincidence circuit and lead sheathing of the case eflect the background is shown in Table II.

A general block diagram of the apparatus is shown in Fig. 3. In this diagram blocks 1, 2, 3, 4 are input forming circuits; block 5 is a circuit registering coincident pulses and subtracting from their number the cosmic background pulses; block 6 is a circuit subtracting cosmic background pulses from the number of pulses registered by the beta counter; block 7 is a circuit mixing pulses from the rings of the gamma counters and subtracting from their number the cosmic background pulses; blocks 8, 9, 10, 11 are output forming elements; SC-64 is a standard scaling device; E.M.C. is a mechanical register.

An assembled view of the apparatus is shown in Fig. 4.

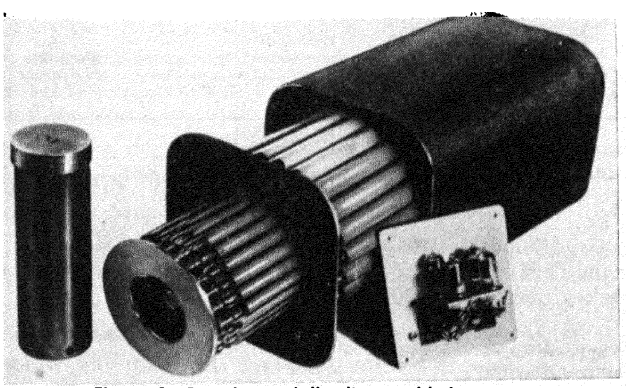

Figure 2. Case in partially disassembled state

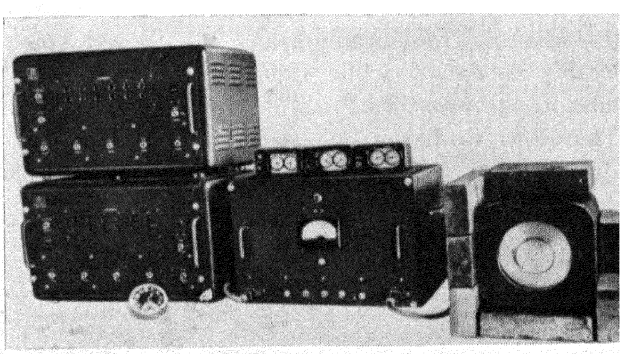

Figure 4. General view of the apparatus

Determining the Parameters of the Apparatus

Formulae were derived for determining the uranium, radium and thorium content in radioactive ores on the basis of the method of measurement considered above.

However, the numerical values of the factors contained in these formulas must be obtained before the latter can be applied for practical determinations. With this in mind, standard samples were made up having a known content of radioactive components and a known weight of rock. Numerous measurements of these samples were made by the apparatus. The factors were calculated from the measured data and have the following values:

$a = 95$ pulses/min-gram%
$b = 48.5$ pulses/min-gram%
$A = 8900$ pulses/min-%
$B = 4440$ pulses/min-%
$C = 4440$ pulses/min-%
$\chi_{Ra} = 1.1\%$
$\chi_{Th} = 2.4\%$

Corrections accounting for the influence of gamma radiation from the sample on the number of counts made by the beta counter must be introduced in order to eliminate errors in determining the uranium content from beta measurements. One can write:

$$N^{\beta} = A^{\beta} R_{Ra} + A^{\Gamma} R_{Ra} + B^{\beta} R_{Th} + B^{\Gamma} R_{Th} + C R_{U}$$

where A^{β}, B^{β}, C are factors accounting for part of the beta radiation from a given element in the general counting balance of beta radiation, and A^{Γ}, B^{Γ} are factors accounting for part of the registered gamma radiation.

Numerical values of factors accounting for gamma radiation can be ascertained indirectly. It is known that the intensity of beta radiation from uranium and from RaC when in a state of equilibrium is approximately the same. The authors of this paper have data showing $A^{\beta}/C = 1.08$. The effect of the weight of the rock is taken into account in the factor A^{Γ} in the following manner:

$$A^{\Gamma} = A_0^{\Gamma} \frac{P}{P_0}$$

where A_0^{Γ} is the value of the factor obtained from standard tests of the apparatus with a given sample of weight P_0. In this case the factor A^{Γ} may be obtained from the relationship given above for the factors A^{β} and C

$$A^{\Gamma} = A - A^{\beta} = A - 1.08C$$

The factors B^{β} and B^{Γ} can then be calculated using the value of the factor A^{Γ} found above.

The ratio b/a was found equal to $b/a = 0.51$. Therefore,

$$B^{\Gamma} = A^{\Gamma} \frac{b}{a} = 0.51 A^{\Gamma} = 0.51 A_0^{\Gamma} \frac{P}{P_0}$$

Making use of the parameters given above we find:

$A^{\beta} = 4750$ pulses/min-%
$A^{\Gamma} = 4150\ P/P_0$ pulses/min-%
$B^{\beta} = 2380$ pulses/min-%
$B^{\Gamma} = 2120\ P/P_0$ pulses min-%

Let us calculate the ratio of factors A^{β}/B^{β} and a/b

$$\frac{A^{\beta}}{B^{\beta}} = 1.99, \frac{a}{b} = 1.96, \frac{A^{\beta}}{a} = \frac{B^{\beta}}{b}(1 + \epsilon)$$

where $\epsilon = 0.018$.

Calculations indicate that a connection exists between counting balance factors of beta and gamma radiations which, by the way, was mentioned earlier.

Table III*

No.	Weight, grams	Content according to chemical analysis	Content as determined by apparatus
1	946	$R_U = 0.002$ $R_{Th} = 0.12$	$R_{Ra} = 0.002 \pm 0.003$ $R_U = 0.004 \pm 0.002$ $R_{Th} = 0.119 \pm 0.01$
2	880	$R_U = 0.004$ $R_{Th} = 0.06$	$R_{Ra} = 0.005 \pm 0.003$ $R_U = 0.006 \pm 0.002$ $R_{Th} = 0.06 \pm 0.005$
3	769	$R_U = 0.002$ $R_{Th} = 0.058$	$R_{Ra} = 0.005 \pm 0.003$ $R_U = 0.003 \pm 0.002$ $R_{Th} = 0.048 \pm 0.005$
4	735	$R_U = 0.07$ $R_{Th} = 0.00$	$R_{Ra} = 0.07 \pm 0.005$ $R_U = 0.08 \pm 0.005$ $R_{Th} = 0.00 \pm 0.003$
5	880	$R_{Ra} = 0.068$ $R_U = 0.062$ $R_{Th} = 0.006$	$R_{Ra} = 0.082 \pm 0.008$ $R_U = 0.068 \pm 0.005$ $R_{Th} = 0.00 \pm 0.003$

* Radium contents in the samples are given in terms of equivalent uranium content.

Results of Testing the Apparatus in the Laboratory and in the Field

Working formulae for determining the uranium, radium and thorium content in radioactive ore are as follows:

$$R_U = \frac{N^{\beta}}{C} - \frac{A^{\beta} + A_0^{\Gamma} \frac{P}{P_0}}{aCP} N^{\Gamma}$$

$$R_{Ra} = \frac{N^{\Gamma}\chi_{Th} - N^{\gamma}}{aP(\chi_{Th} - \chi_{Ra})} \qquad R_{Th} = \frac{N^{\gamma} - N^{\Gamma}\chi_{Ra}}{bP(\chi_{Th} - \chi_{Ra})}$$

where N^{β}, N^{γ}, N^{Γ} are the number of pulses per minute registered by the corresponding channel with the background subtracted; P is the weight of the sample; $A_0^{\Gamma}/P_0 = 5.9$ pulses/min-gram %; $A^{\beta} = 4750$ pulses/min-%; $C = 4400$ pulses/min-%; $a = 95$ pulses/min-gram %; $b = 48.5$ pulses/min-gram %; $\chi_{Ra} = 1.1 \times 10^{-2}$; $\chi_{Th} = 2.4 \times 10^{-2}$; $\chi_{Ra} = 1.3 \times 10^{-2}$; R_U, R_{Ra}, R_{Th} are values of the uranium, radium and thorium contents in the ore, in per cent.

Laboratory results of studies carried out with the apparatus described are given in Table III for five different samples of radioactive ores.

A check was made to test the linearity of the apparatus as a function of the quantitative content of radioactive matter. The composition of the sample in all cases was identical. Checks showed that no deviation from linearity was observed in all three channels for a wide range of counting rates.

After undergoing laboratory tests the apparatus was operated in the field. In July 1954, 110 analyses were performed with the apparatus.

All samples analysed with the apparatus also underwent numerous chemical and radiochemical analyses in different laboratories. At the present we have material on chemical and radiochemical analyses of 88 samples containing from 0.005% to 2% of radioactive elements with different proportions of thorium, radium and uranium content. Results of chemical and radiochemical analyses of the 88 samples compare well with results given by the apparatus.

It should be noted that chemical and radiochemical analyses for uranium, radium and especially thorium require many days of labor of highly qualified chemists. Analyses of a sample with the apparatus developed takes from 5 to 50 minutes (depending upon the percentage content of radioactive matter). The apparatus is handled by operators having low qualifications. The relative accuracy of measurement comprises from 5 to 10% of the content of the unknown component when the content is greater than 0.01%.

CONCLUSION

The possibility of determining uranium, radium and thorium content in radioactive ores by means of simultaneous measurements of their beta and gamma radiation is shown in the paper.

Experiments showed that the simplest solution to the problem can be obtained by means of threshold spectrometry of gamma radiation.

An apparatus was designed and constructed that made possible a single and simultaneous determination of uranium, radium and thorium content in radioactive ores based on measurements of beta and gamma radiation.

Use of this apparatus in practice for geophysical studies showed the high efficiency of the proposed method. Data of chemical and radiochemical analyses of samples compare well with data given by the apparatus.

Thus, the first few experimental studies concerning the practical application of the apparatus allow one to hope that the method developed and the apparatus based on it will find wide use in geological and mining work in the uranium extracting industry.

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Analysis of Mixed Uranium and Thorium Ores by the Measurement of Gamma Radiation

By A. M. Baptista and J. Palacios,* Portugal

In a previous paper (Revista de Faculdade de Ciências de Lisboa, 2a, serie, 2, 49, 1952) we described a method for the analysis of radioactive minerals. Our method was based on the fact that, under certain circumstances, the response of a Geiger-Müller detector is proportional to the mass of the mineral used in the measurements. Our intention now is to make a more complete study of this method and to ascertain whether it can be used to determine the contents of uranium and thorium in minerals where both elements are present.

Figure 1 shows the apparatus used. It includes a lead cathode detector tube filled with a mixture of argon and alcohol. The 25 cm long cathode gives a *neutral zone* of about 14 cm. After pulverization, the ore is placed in an 11 cm-high double walled Pyrex container, with a distance of 11 mm between walls. This unit was placed in a 3 cm-thick lead shield. With this instrumentation, background was about 170 cpm.

Figures 2 and 3, obtained with samples of uranium ore and with uranium + thorium ore, show an ideal ratio between the cpm and the mass used, although the apparent densities had varied between 1.2 and 2.3 gm/cm^3.

THE BASIS OF THE METHOD

We shall assume an ore containing uranium and thorium to be in equilibrium with all the members of their respective families and that both emanations, Rn and Tn, are extracted as they are formed, the reaction lasting for a time, θ. The glass is covered to prevent the gases escaping, and the gamma activity is measured as a function of time. From the study of the uranium and thorium families,† taking into consideration the half-life of the different members and limiting ourselves to the gamma emitters descended from both emanations, it follows that, in the case of uranium, the activity diminishes during the extraction because of the reduction in the number of atoms of RaA, RaB and RaC, (Fig. 4), and tends toward zero when the extraction is prolonged indefinitely. Hence, the initial activity during the second stage, i.e., when the release of emanation is obstructed, depends on time, θ.

During the recovery stage, radioactivity continues to decrease, it reaches a minimum, then slowly increases, and as shown on Fig. 5, causes the minimum

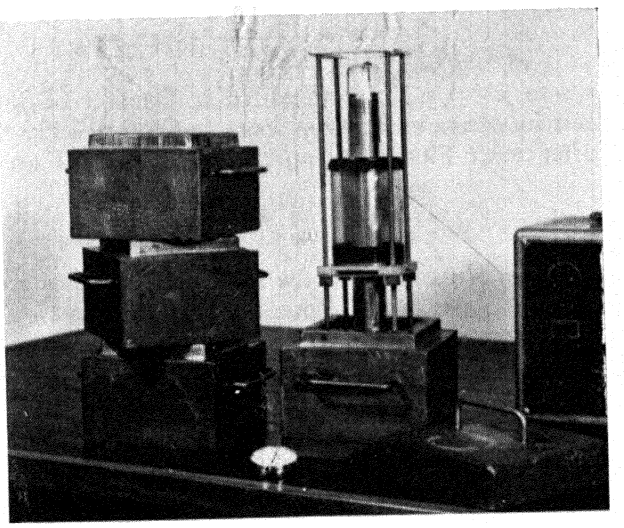

Figure 1. Apparatus for analysis of radioactive ores

value of the relative activity, $a_U = A_U/A_\infty$, to be practically independent of extraction time θ, so that a 10-minute extraction of the radiation is sufficient to reduce the minimum to $a_U = 0.03$, although it is $a_U = 0.9$ at the end of extraction.

Since the behavior of the thorium family is entirely different, it should be possible to detect its presence in the mixture.

In effect, the decrease in activity during the first stage is much slower than for uranium, and a one hour extraction of emanation is sufficient for bringing the relative activity to $a_T = A_T/A_\infty = 0.82$. Moreover, since the thorium is very short-lived; its daughters are born so fast that the recovery curve rises from the first moment. The quantitative study revealed other facts, very favorable for our purpose.

Since radon is much longer-lived than any of its gamma emitter daughters, all the recovery curves, regardless of θ, may for practical purposes be considered as coinciding after $t = 3$ hours, the time t being measured from the instant in which the emanation flow was observed (Fig. 5) and the formula

$$a_U = 1 - \exp(-\lambda t) = f(t) \qquad (1)$$

is valid. As could be expected, there is no other

Original language: Spanish.

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† The complete study was done by J. M. Cayolla Carpinteiro, whom we thank for his valuable cooperation.

parameter besides the decay constant of radon, $\lambda = 0.1812\ d^{-1}$.

In contradistinction, the recovery curve of the thorium family depends on extraction time, θ, and is described by the equation:

$$\alpha_{Th} = [- \exp(-\lambda'\theta)] \exp(-\lambda' t) = \phi(t,\theta) \quad (2)$$

where $\lambda = 1.099 \times 10^3\ d^{-1}$ is the disintegration constant of thoron. This value of λ' accounts for the rapid growth of α_{Th} so that recovery is almost completed after a few hours.

Applying Equations 1 and 2, the recovery curve of an ore containing X grams of U_3O_8 and Y grams of ThO_2 per gram is easily constructed. In effect, if x is the fraction which the radon daughters contribute to the total radiation, we have:

$$x = \frac{a - 1}{f(t) - 1} \quad (3)$$

where $a = n/n_\infty$, expressed as a fraction of the activity of the equilibrium stage, is the total activity after time t. Finally the expressions for X and Y are:

$$X = \frac{x n_\infty}{\xi m}; \qquad Y = \frac{(1 - x)\, n_\infty}{\eta m} \quad (4)$$

where m is the mass of the sample and ξ and η are the counts per minute, corresponding to 1 gm U_3O_8 and to 1 gm ThO_2, respectively.

To find n directly, it is necessary to wait until the sample recovers its radioactive equilibrium since a considerable loss of radiation occurs during grinding. This difficulty is avoided by taking two measurements at t_1 and t_2, conveniently chosen, and applying the formula:

$$n_\infty = \frac{n(t_2)\,[1 - f(t_1)] - n(t_1)\,[1 - f(t_2)]}{f(t_2) - f(t_1)} \quad (5)$$

EXPERIMENTAL METHOD

Of the methods tested for the expulsion of the emanations, a simple and quite satisfactory one consists of placing the sample in a double walled glass vessel where measurements are taken and, after weighing, attacking it with aqua regia with moderate boiling for a time $\theta = 1$ hour when the ore falls to pieces and the emanation is carried away by the bubbles. The glass vessel is then covered and the recovery stage begins. Measurement of the cpm can be started after three hours.

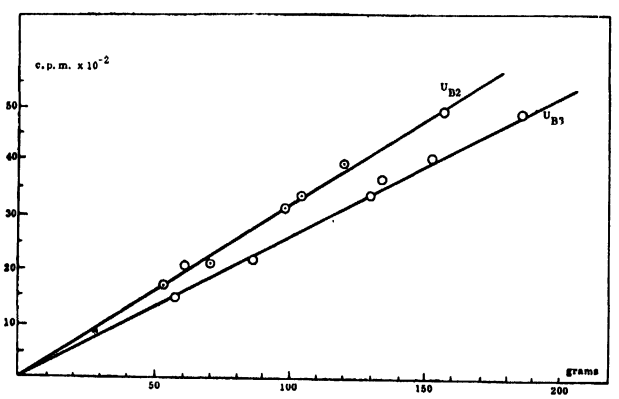

Figure 2. Ratio of detector readings (cpm) to ore mass (uranium)

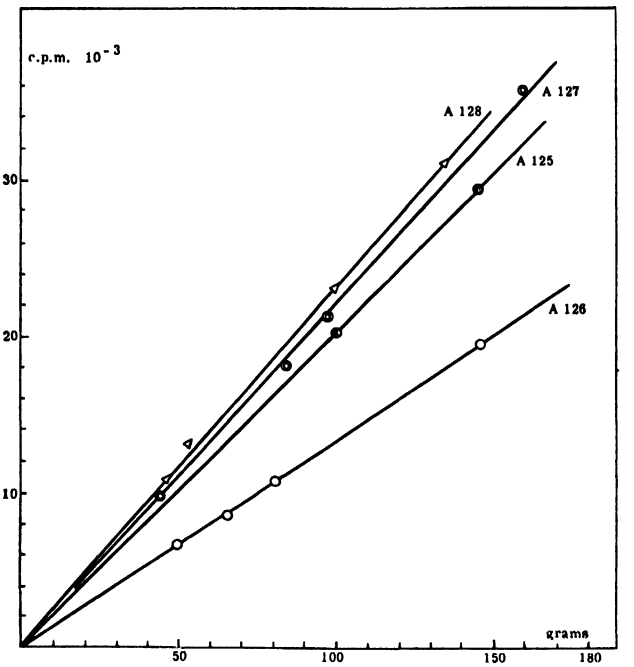

Figure 3. Ratio of detector readings (cpm) and ore mass (uranium and thorium)

RESULTS

To test our method we applied it to an ore, free from thorium and having a known uranium content. The points surrounded by circles in Fig. 6 refer to a sample containing 1.45% of U_3O_8 and curve I is the theoretical curve based on Equation 1. The regular discrepancy observed is well beyond any possible errors of measurements. Thus, the minimum anticipated for the extraction time of 1 hour is 0.03, while the experimental value was 0.16; and this value was reproduced upon repetition of the operation under the same condition with different ores and varying the extraction time between 1 and 3 hours.

There may be two causes for this discrepancy; first the incomplete extraction of radon, and second, the failure to take into consideration the gamma radiation of the members born before the radon. It is easy to see that both reasons will affect the radioactivity constant, ϵA_∞, in such a way that instead of the minimum of the curve 0 for $\theta = \infty$ it is converted to ϵ.

To take this condition into account it suffices to remember that the variable part is αA_∞, in which $\alpha = 1 - \epsilon$, which in view of Equation 1 gives:

$$n/n_\infty = 1 - \alpha \exp(-\lambda t) \quad (6)$$

We have attempted to find how both causes affect the value of the fraction $1 - \epsilon$. It must be kept in mind that, after the attack, there remains in the glass a granular deposit resembling the sample before the treatment with aqua regia; this deposit is covered with a light precipitate which spreads

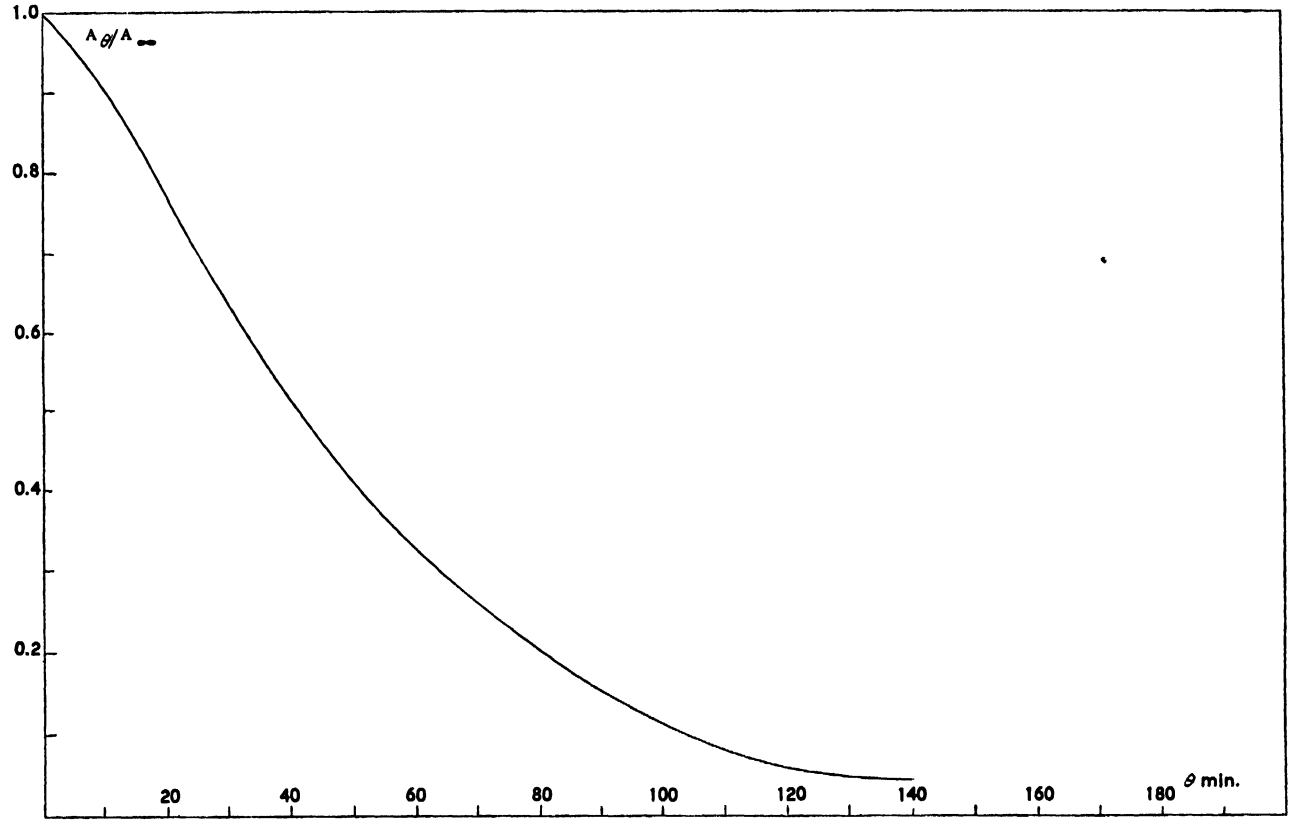

Figure 4. Theoretical curve of the relative activity $A\theta/A_\infty = n\theta/n_\infty$ of a uranium ore after extraction, during time θ

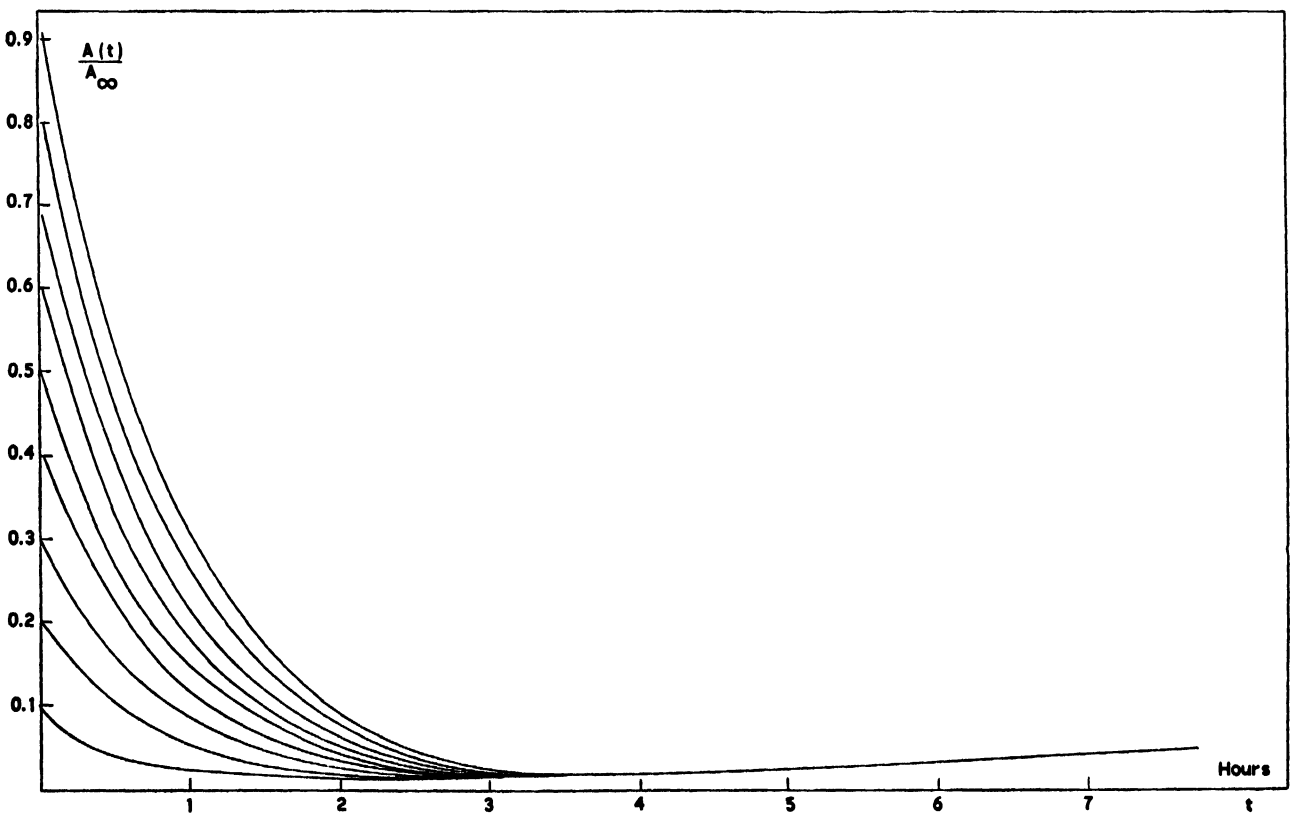

Figure 5. Theoretical recovery curves of uranium ores activities for different values of extraction time θ

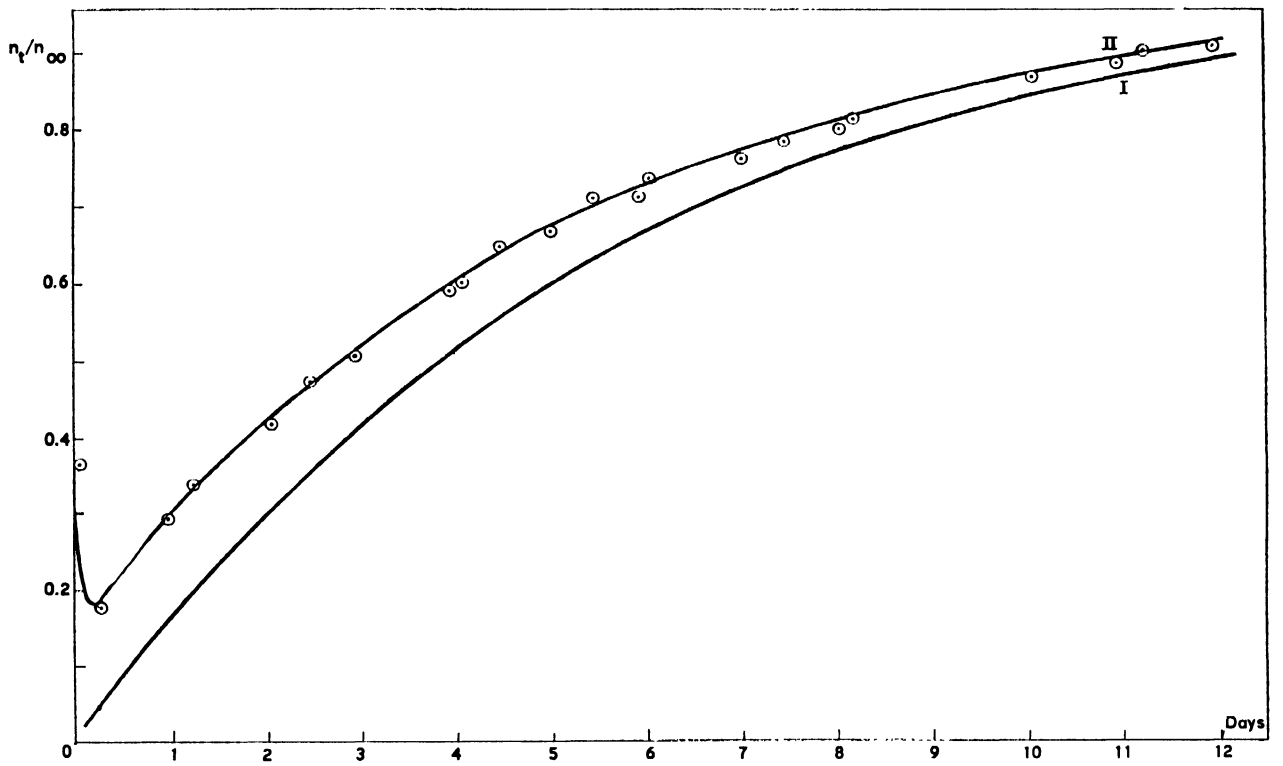

Figure 6. Recovery of the activity of uranium ore (1.45% U_3O_8) after treatment for one hour with boiling aqua regia. The circles represent experimental values. Curves I and II were constructed from Equation 6 in which α 1 and $\alpha = 0.84$, respectively

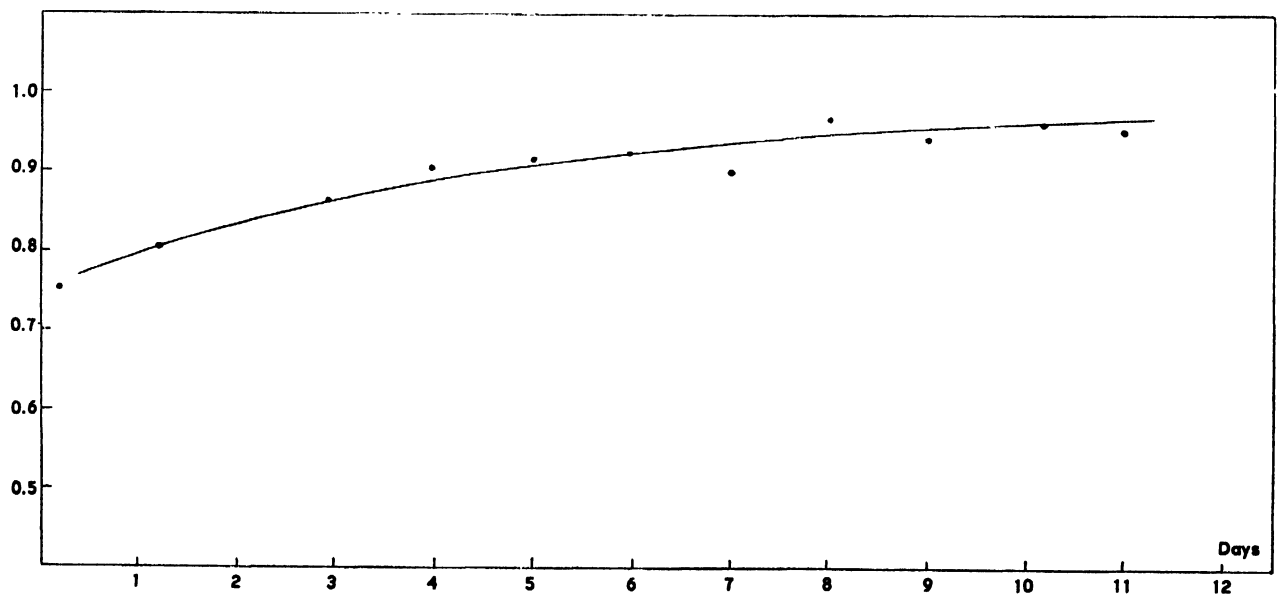

Figure 7. Recovery of activity of a uranium ore whose radioactive equilibrium had been disturbed by grinding and subsequent handling

throughout the liquid upon stirring. By adding water, separating the precipitate with a pipette and repeating the extraction of radon, it is possible to reduce the remaining activity to $\epsilon = 0.12$. This slight drop (from 0.16 to 0.12), obtained with such a substantial difference in grain size, would suggest that the greater part of the remanent activity is due to the gamma emitters preceding the radon. In any case, the persistent continuity of the minimum value under very different conditions makes it possible to use the value $\alpha = 1 - \epsilon = 0.84$ for all practical purposes. With this value, and using Equation 6, curve II has been constructed from Fig. 6 and as may be seen, the agreement is perfect.

As we have already seen, ore grinding causes considerable release of emanation; the same applies to the upsetting of the powder. The recovery formula, Equation 6, can be verified without treating the ore chemically. In the example in Fig. 6 a minimum of $\epsilon = 0.75$ was obtained simply by stirring, and we can see that its curve agrees well with the experimental values.

FORMULAE FOR DETERMINING CONTENTS OF MIXED ORES

Considering the remaining activity and the fact that the function $\phi(t)$ is practically unity for $t > 3$ hours, Equations 1 and 2 lead to:

$$n(t)/n_\infty = x[1 - \alpha \exp(-\lambda t)] + (1 - x)$$

or:

$$n(t)/n_\infty = 1 - \alpha' \exp(-\lambda t) \qquad (7)$$

in which:

$$\alpha' = x\alpha \qquad (8)$$

and since $\alpha = 0.84$, it suffices to solve for α' in order to compute x. This is obtained with two measurements of n, since Equation 7 gives:

$$\alpha' = \frac{n(t) - n(t_1)}{n(t) \exp(-\lambda t_1) - n(t_1) \exp(-\lambda t)}$$

To be able to apply Equation 4, it is necessary to find the values of ξ and η, which requires calibrating the counter in order to find the cpm for 1 gm U_3O_8 and ThO_2, respectively. This operation requires ores of a known composition.

Table I gives the results obtained with several ores free from thorium.

Table I. Adjustments of the Detector Tube

Mass (gm)	n_∞ cpm	% U_3O_8	$\xi \times 10^{-3}$ (cpm /gm U_3O_8)
35	1342	1.45	2.64
35	1214	1.32	2.63
35	1470	1.53	2.74

With a mixed uranium and thorium ore, the results of the measurements are given in Table II.

Table II. Uranium and Thorium Ore

t (days)	$n \times 10^{-3}$ (cpm)	$exp(-\lambda t)$	α'
0.125	2.82	0.978	—
0.96	3.08	0.840	0.61
1.96	3.30	0.711	0.58
3.04	3.55	0.589	0.60
3.87	3.89	0.510	0.58
		Average	0.55

With $\alpha' = 1 - \epsilon' = 0.42$, and using the accepted value of α, we get:

$$x = \frac{\alpha'}{\alpha} = \frac{0.42}{0.84} = 0.50$$

On the other hand, from the figures in the table, we obtained:

$$n_\infty = \frac{n(t)}{1 - \alpha' \exp(-\lambda t)} = 4.79 \times 10^3$$

whence, since ξ is known, and using Equation 4, we have

$$X = 0.0247 \text{ gm } U_3O_8/\text{gm ore}$$

This proves that it is sufficient, in order to find the uranium content in a mixed ore, to calibrate the tube for uranium. Since we have no available data for an ore with a known thorium content, the comparison of our results with those obtained by chemical methods will have to be done in the future.

ACKNOWLEDGEMENTS

We express our appreciation to Professor Herculano de Carvalho for his contribution of several samples of Portuguese radioactive ores. We also thank Dr. R. Libano Monteiro and laboratory technician F. Alves Martins for their measurements which have so greatly helped us in this work.

Determination of the U^{235} Content in Uranium by a Radiochemical Method

By I. G. de Fraenz and W. Seelman-Eggebert,* Argentina

For the method described here, we assume that the isotopic ratio (U^{238}/U^{235}) in natural uranium is known. The measurements of Dempter,[1] Nier[2] and Kienberger[3] carried out with the mass spectrometer gave a value of 140 ± 1 for this ratio. In addition to the use of the mass spectrometer for the determination of the U^{235} content, α particle measurements can also be used for analysis of the ratio of U^{235} fission to U^{239} formation by thermal neutrons.

α measurements are not useful for very low U^{235} contents, and for uranium fission, neutrons must be available. On the other hand, however, the radiochemical method is suitable for use with the means normally available in a specialized laboratory.

The radiochemical method consists of a comparison of the activities of the daughter products of the two uranium isotopes U^{238} and U^{235}. These two isotopes disintegrate with the emission of alpha particles, with long half-lives, to give the thorium isotopes UX_1 and UY, which are β-emitters having comparatively short half-lives (24.1 days and 25.5 hours). If U is radiochemically separated from its daughter products, the two isotopes of thorium will again form the parent substance.

Due to its shorter half-life, the activity of UY will develop much more rapidly than that of UX_1, so that, shortly after separation, the ratio between these activities changes in favor of the UY fraction.

If the isotopes of thorium are separated from uranium at time $t = 0$, we shall again have, according to the known formulae of radioactive disintegration:

$$A(UX_1) = \lambda(U^{238}) \cdot N(U^{238}) \cdot (1 - e^{-\lambda(UX_1)t})$$

$$A(UY) = \lambda(U^{235}) \cdot N(U^{235}) \cdot (1 - e^{-\lambda(UY)t})$$

where $A(UX_1)$, $A(UY)$ = absolute activities of UX_1 and UY, respectively, found in the sample; $\lambda(UX_1)$, $\lambda(UY)$, etc. = disintegration constants of UX_1 and UY respectively; $N(U^{238})$, $N(U^{235})$ = number of atoms of U^{238} and U^{235} respectively.

Using the half-lives, rather than the disintegration constants:[4]

$$\lambda(U^{238}) = \frac{\ln 2}{4.49 \times 10^9} \text{ and } \lambda(U^{235}) = \frac{\ln 2}{7.13 \times 10^8}$$

we obtain, for the ratio of the activities:

$$\frac{A(UY)}{A(UX_1)} = \frac{1}{Q_y} \cdot \frac{4.49 \times 10^9 \cdot (1 - e^{-\lambda(UY)t})}{7.13 \times 10^8 \cdot (1 - e^{-\lambda(UX_1)t})} = \frac{6.31}{Q_y} \cdot \frac{1 - e^{-\lambda(UY)t}}{1 - e^{-\lambda(UY_1)t}} \quad (1)$$

The relation between the activities of the two daughter products depends on the time of formation. In Fig. 1 this dependency is shown for natural uranium ($Q_y = 140$). In radioactive equilibrium, the ratio is equal to 0.045. Conversely, when extrapolating to the moment of the separation, it is 1.02. When the time elapsed from the last separation and the ratio of activities of the daughter products is known for an unknown mixture of isotopes, it becomes possible to find the isotopic relationship sought, Q_y, by means of Equation 1, or Fig. 1.

The fact that both UX_1 and UY have complex β-radiation spectra of low maximum energy makes it difficult to measure in practice the ratio of activities. For UX_1 a figure of 0.205 Mev (80%) is given as well as 0.111 Mev (20%)[5] and for UY, 0.302 Mev (44%), 0.216 Mev (11%) and 0.094 Mev (45%).[6] A hard beta radiation (2.32 Mev), is superimposed on this soft radiation, due to the daughter product of UX_1 (UX_2) which, with a half-life of 1.14 minutes, practically always is in equilibrium with UX_1. Therefore, it is not possible to measure directly the ratio of the activities sought, and one has to go into comparative measurements.

From a preparation which contains UX_1, UX_2 and UY, the measurements do not bear on the absolute activities of the 3 nuclides, but rather on a fraction of them. This fraction depends on the measuring device used, the energy of the radiation emitted by the nuclides, and the shape and thickness of the preparation itself. Designating the efficiency of the activity detection for UX_1 by α, for UX_2 by β and for UY by γ, the total measured activity will be:

$$\alpha A\,(UX_1) + \beta A\,(UX_2) + \gamma A\,(UY)$$

Placing a sheet of aluminum approximately 30 mg/cm² on the preparation the soft radiation of UX_1 and UY is completely absorbed, so that only a fraction $\delta \cdot A(UX_2)$ of the absolute activity of the UX_2 is measured. If the preparation, which contains UX_1, UX_2 and UY, is measured with and without an aluminum plate, the quotient of the two results of the measurements will be:

Original language: Spanish.

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$$Q_1 = \frac{\alpha A(UX_1) + \beta A(UX_2) + \gamma A(UY)}{\delta A(UX_2)}$$

If $A(UX_2) = A(UX_1)$, since UX_1 and UX_2 are in radioactive equilibrium, we shall have:

$$Q_1 = \frac{\alpha + \beta}{\delta} + \frac{\gamma}{\delta} \cdot \frac{A(UY)}{A(UX_1)}$$

In a preparation which contains UX_1, UX_2 and UY, UY disintegrates more rapidly than UX_1 so that, at the end of the week, we have only UX_1 and UX_2 in this preparation. Computing the quotient for this preparation, as we did above, we get:

$$Q_2 = \frac{\alpha A(UX_2) + \beta A(UX_1)}{\delta A(UX_2)} = \frac{\alpha + \beta}{\delta}$$

The difference between the quotients

$$Q_1 - Q_2 = (Y/\delta) \cdot [A(UY)/A(UX)] \quad (2)$$

gives the ratio between activities sought, multiplied by factor Y/δ. This factor, which depends on the measuring devices used, is determined with natural uranium.

DETAILS OF DETERMINATION

The U sample to be studied is dissolved in 25% HCl (approximately 10 gm uranium).

The solution must not contain any extraneous activities or oxidizing substances.

By adding a few milligrams of zirconium as a carrier, the various isotopes of thorium can be precipitated hot with sodium hypophosphate and filtered using a colloidal filter. Precipitation is repeated, again adding zirconium, until the activity of the precipitate corresponds to that formed in the time elapsed between the last two precipitations. After 4 to 8 hours (according to the time available), the uranium solution is divided into 3 to 5 parts and, from each part, the thorium isotopes again formed in the meantime are separated. In order to reduce the self-absorption effect in the preparation, only 0.1 mg of Zr will be used as a carrier for this precipitation, which does not have to be quantitative. In view of the soft radiation, the preparation must be measured very close to the counting tube, so that the geometry of the device must be of the readily reproducible type. For this reason is placed on the 40 mm diameter Buchner funnel customarily used, a glass cylinder 21 mm in diameter with a ground edge and a ring is printed (using ink of the pad type) on the colloidal filter before filtration. In this way, when the filtration is carried out, the limit of the precipitate, itself nearly invisible, will be clearly seen through the glass. The colloidal filter, which is still wet, is fixed over an opening made in a sheet of lucite. Upon drying, the colloidal filter is completely flat and the colored ring is not deformed, and in this manner the preparate can be perfectly centered. It is not necessary to fix the precipitate, for in such small quantities as in this case, it adheres perfectly to the colloidal filter.

Following drying, the precipitate is measured very close to the window of a thin window bell type counting tube. Since UY loses 2% of its activity within an hour, the time between the precipitation and measurement must be short and constant for all these measurements. For a low U^{235} content, the probable statistical error should not be any greater than 0.5%; to this end, it is necessary to take approximately 20,000 counts each time. The preparation is measured consecutively with and without an Al plate, and after the background is subtracted and the dead time correction made, the quotient of the two measurements is computed. In order to obtain accurate results, precipitation and measurement are repeated 3 to 5 times.

For each quotient, the value corresponding to time $t = 0$ is obtained by extrapolation with the help of curve 1, and the mean, Q_1, of these values is then computed. From this, one must subtract the quotient of the standards. As a standard, an old preparation may be used (must be more than 6 days old), or again a preparation may be made by precipitating direct, without any preliminary purifying, the UX_1, UX_2 and UY from a uranium solution which is in a radioactive equilibrium. The standard is measured with and without an Al sheet at the beginning and at the end of each series of measurements. It must be kept in a dry, dust free place, and must be prepared fresh approximately once a month.

A determination is then made, in the form indicated, of the average Q_1 for natural uranium, the

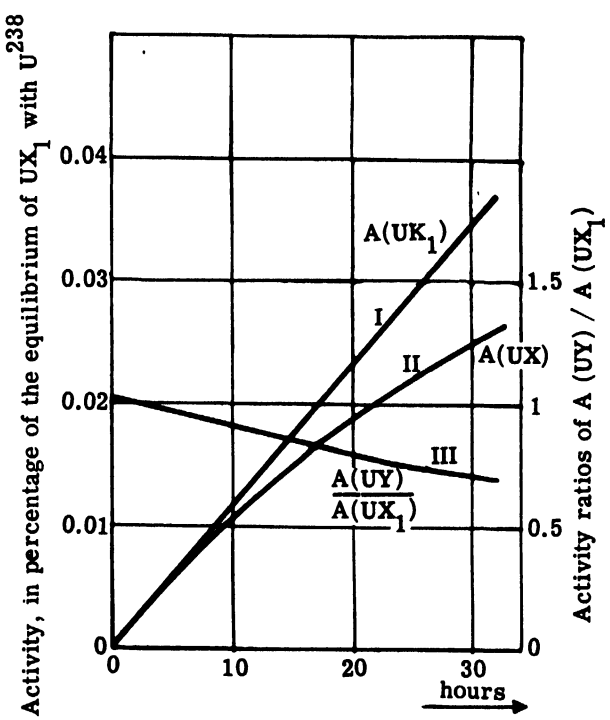

Figure 1. Increase in the activity of UX and UY in natural uranium as a function of the time elapsed from the moment of purification of uranium. Curve 1 indicates the activity of UX, curve II that of UY and curve III the ratio of the activities of UX and UY in natural uranium

quotient of the standard is subtracted, and the characteristic constant for the device is computed:

$$\frac{\gamma}{\delta} = \frac{Q_1 - Q_2}{1.03} \text{ with } 1.03 = \frac{A(\mathrm{UY})}{A(\mathrm{UX_1})}$$

for natural uranium at time $t = 0$.

This calibration value will have to be measured periodically by way of a check-up on the device.

The unknown uranium sample is studied in the same fashion, after which the difference $Q_1 - Q_2$ is determined.

The absolute activity ratio, between UY and UX_1 according to Equation 2 is

$$\frac{A(\mathrm{UY})}{A(\mathrm{UX_1})} = \frac{\delta}{\gamma}(Q_1 - Q_2)$$

The isotope ratio, therefore, will be:

$$Q_y = \frac{A(\mathrm{UX_1})}{A(\mathrm{UY})} \times 6.37 \times \frac{\lambda(\mathrm{UY})}{\lambda(\mathrm{UX_1})} = 144 \times \frac{A(\mathrm{UX_1})}{A(\mathrm{UY})}$$

EXAMPLE OF THE ANALYSIS OF DEPLETED URANIUM

We had neither enriched nor depleted uranium to try out the method described. Since all the methods in existence give an easier determination of the U^{235} content of an enriched, than of a depleted sample, the most interesting value of the method is in its application to low U^{235} contents.

A depleted uranium sample can be prepared in the following way: on separating the isotopes of thorium from once purified uranium, not as in the experiment described above but later (i.e., shortly after the first purification, when the ratio of UY and UX_1 activities is still large), we shall have a smaller ratio of activities similar to U^{235} depleted uranium as processed in the normal way. From Fig. 2, it is possible to determine the time which should elapse between the first and second precipitation in order to obtain uranium which contains 1/1000, 2/1000 and up to 7/1000 of U^{235}.

Isotopic ratio	*Time elapsed between the 1st and 2nd precipitations*
1/1000	323 hours
2/1000	138 hours
3/1000	82 hours
4/1000	50 hours
5/1000	29 hours
6/1000	14 hours

If the thorium isotopes are separated from a series of uranium solutions, each in two stages and with different time intervals between the first and second separation, and if the quotients of the activities are represented as a function of the time intervals, it will be possible to test the suitability of the method for a comparison of the results so obtained against the theoretical curve. The points represented on Fig. 2 are the results of such a series of measurements, and show that for a U^{235} depleted uranium it is possible to differentiate between U^{235} contents of 0 and 1%, and 1% to 2%, respectively.

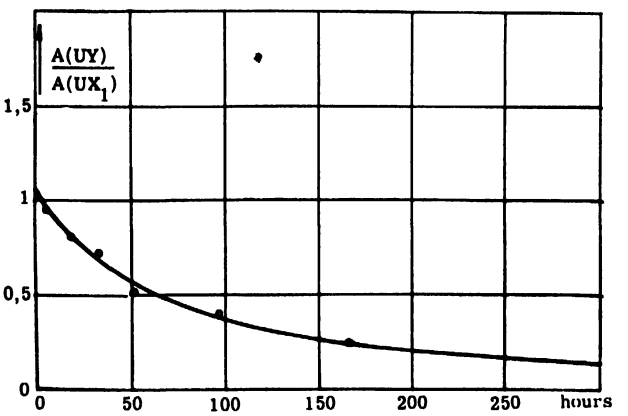

Figure 2. A(UY)/A(UX_1) for natural uranium as a function of the time for the two daughter products to form again. The points give the results of a model test

Should this be necessary, the error made on the measurement can be reduced further by using a constant dead-time device, and by increasing the number of control measurement from which the average value is taken.

DISCUSSION OF THE PRECISION OF THE METHOD FOR ENRICHED URANIUM SAMPLES

The relative error with which the quotient of the isotopes is obtained will be all the greater as the U^{235} content of the substance is smaller. Therefore, the quantity of uranium to be analyzed must be as large as possible to give a satisfactory UY activity.

On the other hand, in order to analyze enriched uranium, it is possible to work with smaller quantities, and the relative error can be decreased down to 2%.

Now, by way of example, a discussion is given below of the analysis of a uranium sample, the U^{235} content of which is 30%. Before the substance mentioned is analyzed, the equipment must be calibrated with natural uranium; this can be done with 10 gm of uranium approximately, divided into 3 parts following the first purification. If separation is made 7 hours later, one obtains approximately 2000 cpm of the activity which pertains to UX_2. This value corresponds to a measurement with an absorption sheet, without which one would obtain about 5000 cpm which would correspond to activities of UX_1, UX_2 and UY. Making a half hour measurement, quotient Q_1 is obtained with an accuracy of 0.7%. Experience has shown that the additional errors which affect the results are of the same order. By repeating the measurement three times, the error can be reduced to 1%. It is necessary to work with a very active standard so that the measuring take little time and can be repeated many times. The values so obtained vary by 1%. The factor γ/δ, which is the difference of the two quotients, is obtained with an accuracy of 3%. The size of this error will be understood, allowing for the fact that the efficiency of a G-M tube must be measured for a very soft radiation.

The error can be reduced by using for calibration, an enriched uranium solution the U^{235} content of which is exactly known. A solution of 3 gm uranium with 5% U^{235} is recommended. After the first purification, the calibration solution is divided into 3 equal parts which each give at the end of 24 hours, 6000 cpm and 1300 cpm, measured with and without absorbing plates respectively.

Quotient Q_2 is determined from the three preparations with an accuracy of 1%. This gives an error, for factor γ/δ, of 1.3%.

The essential problem in the analysis of enriched uranium does not reside in an artificial increase in the activity coefficient of UY and UX_1, since this coefficient in the case of uranium containing 30% of U^{235} is 44.2 immediately after the first purification, 33.7 after one day, 26.15 at the end of two days, and finally 1.93 under conditions of equilibrium.

This means that the error in the analysis does not depend on the time elapsed between the two purifications, but rather on the error in the measurement of the denominator, conditioned by the activity of UX_2 which must be sufficiently large.

The error in the standard which greatly influences the analysis of depleted uranium is not very significant in the case of an activity coefficient greater than 5.

Using a total quantity of 1 gm of uranium sample which will be used for 3 simultaneous measurements, and separating for the second time 24 hours after the first separation, we obtain approximately 800 cpm of activity which correspond exclusively to UX_2, while the activity going with UX_1, UX_2 and UY is approximately 30,000 cpm. With these activities, it is easy to determine Q_1 within 1%. In the case of calibration with natural uranium, a 3.5% contribution is made to the error in the isotopic valuation, and a 2% error where enriched uranium has been used for the calibration.

For a much smaller quantity, for instance 10 mg, the isotopic coefficient of which must be determined, it is necessary to wait longer for a satisfactory UX_1 activity to be formed; 7 mg of U^{238} gave after 5 days, 100 cpm, while after the same period, 3 mg of U^{235} produced more than 1000 cpm. The corresponding quotient can be determined within 2%. Waiting until the second preparation is made, in order for simultaneous measurements to be possible, the error can be brought down to 1%.

Since use is made of natural uranium, it has not been possible, until now, to obtain experimental data on the analysis of enriched uranium.

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Determination of Microgram and Submicrogram Quantities of Thorium by Neutron Activation Analysis

By G. W. Leddicotte and H. A. Mahlman,* USA

The high neutron intensities found in a chain-reacting pile, such as the Oak Ridge National Laboratory graphite reactor make it possible to determine small amounts of most of the stable elements by the neutron activation analysis method.[1] In this method, the stable isotope(s) of an element, when bombarded by the neutrons of the reactor, will produce an artificial radioisotope (or radioisotopes) of that element. The radionuclide(s) usually formed in the greatest abundance are those produced by the n,γ reaction, the simple neutron capture process. In this process, upon capture of the neutron, gamma rays are emitted and the primary radionuclide produced has the same atomic number as the stable element undergoing the nuclear reaction.

The usual techniques followed after the discharge of the sample from the reactor employ a radiochemical separation of the radionuclide(s) and a measurement of the separated radioactivity by some type of counter.[2-7] The concentration of the stable element in the sample is usually calculated by comparing the radioactivity of the sample with the radioactivity of a comparator sample containing a known amount of the element. In certain analyses, a chemical separation is not necessary and the radioactivity of the radionuclide(s) of interest can be determined by ascertaining the energy of the emitted particle and/or by decay measurements.[7] The limits of detection for the neutron activation analysis method are usually in the range of 1.0 to 0.00001 parts per million or less.[1]

THE DETERMINATION OF THORIUM BY NEUTRON ACTIVATION ANALYSIS

Microgram and submicrogram amounts of thorium can be determined in synthetic materials, ores, clays and mud from river bottoms by neutron activation analysis. The nuclear reaction used in these assays is

$$Th^{232}\ (n,\gamma)\ Th^{233} \xrightarrow[23.3\ min]{\beta^-,\gamma} Pa^{233}\ (27.4\ d) \qquad (1)$$

In this reaction, the formation of Th^{233} in the neutron bombardment is accompanied by the growth of Pa^{233} from the Th^{233} previously formed. If the intensity of the neutron flux of the reactor is assumed to be constant, then the production of Th^{233} in an irradiation is given by the equation

$$A_1 = Nf\sigma S \qquad (2)$$

where A_1 is the Th^{233} activity in disintegrations per second, N is the number of Th^{233} atoms being irradiated, f is the flux in neutrons/cm^2/second, and λ is the activation cross section of Th_{232} in cm^2. S is the "saturation" factor $1 - e^{-\lambda t}$, or the ratio of the amount of Th^{233} radioactivity produced in time t to that produced in infinite time. The decay constant, λ, is related to the half-life of the radionuclide (Th^{233} in this instance) produced ($\lambda = 0.693$ per half-life).

The growth of Pa^{233} during the irradiation is given by the equation

$$A_2 = \frac{(C)\,(f)\,(N)\,(\sigma)}{\lambda_2 - \lambda_1} \times [\lambda_2 - \lambda_1 \cdot\cdot \lambda_2 e^{-\lambda_1 t_1} + \lambda_1 e^{-\lambda_2 t_1}] \qquad (3)$$

where A_2 is the disintegration rate of the Pa^{233} after an irradiation of time t_1, λ_2 is the decay constant of Pa^{233} (27.4 d), and C is the fraction of Th^{233} disintegrations which results in the direct formation of Pa^{233}. Since the half-life of Th^{233} (23.3 min) is so short, essentially all of the radioactivity, following a decay of 4.5 hours after a sample was discharged from the reactor, would be Pa^{233}.

As Pa^{233} decays, it emits both beta and gamma radiations. The radionuclide has thirteen gamma quanta,[8] with an energy range of 0.029–0.416 Mev, which can be conveniently detected by means of a gamma scintillation counter having a sodium iodide (thallium-activated) crystal.[9]

The disintegration rate of Pa^{233} measured by gamma counting is directly proportional to the initial amount of Th^{232} in the sample. The amount of Th^{232} can be calculated by considering the neutron flux at which the sample was irradiated and the decay scheme of the radioisotope produced. The flux intensity may be determined by exposing a monitor containing an element of known activation cross section and half-life at the same time and in the same position in the reactor.

A more simple and accurate method involves the simultaneous irradiation of a known amount of thorium along with the unknown samples. The Pa^{233}

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radioactivity isolated from the thorium comparator and from the unknown sample is corrected to some convenient time to eliminate any error due to decay, and the simple proportion shown below is used to calculate the thorium concentration of the unknown.

$$\text{Weight of thorium in sample} = \frac{\text{Activity of } Pa^{233} \text{ per unit weight of thorium in comparator}}{\text{Activity of } Pa^{233} \text{ in sample}} \quad (4)$$

Since the activation cross section of thorium-232 for thermal neutrons is high, the flux depression, i.e., "self-shadowing," at the center of the sample has been recognized. In this effect, the number of neutrons striking a thick target of thorium will be less than that at the outside of the sample. Thus, the number of neutrons, f, bombarding a point at a distance ΔX from the outside of the target can be determined by the equation:[10]

$$f = f_0 e^{-\sigma N x \Delta X} \quad (5)$$

where f_0 is the number of neutrons bombarding the outside of the target, σ is the cross section of thorium in cm^2/atom and N_X is the density of the sample in atoms/cm^3.

The average number of neutrons to which the sample was exposed can be obtained by integrating Equation 5 between the limits 0 and ΔX. This correction for self shadowing is negligible in the analyses reported below, since the solid samples were irradiated in quartz tubing of 4.0 millimeters internal diameter, and the neutron attenuation was approximately the same for each of the samples.

THE ANALYSIS OF SAMPLES CONTAINING THORIUM BY NEUTRON ACTIVATION ANALYSIS

Irradiation of Sample Materials

Solid Samples

Weighed portions of the sample and of the comparator sample (as thorium nitrate) are placed into small quartz tubes, 0.75 inch long × 6.0 millimeters in diameter (4 mm id). The tubes are capped with a cork stopper wrapped in 2S aluminum and placed in an irradiation container. The irradiation is made for some predetermined time, dependent upon the estimated concentration of the thorium present and the sample size. After discharge from the reactor, the irradiated samples are allowed to decay 4.5 hours before being chemically processed by the basic method described below.

Liquid Samples

Aliquots from the sample and a solution of the thorium comparator are pipetted into polyethylene bottles (0.5–1.0 ounce). The bottles are placed into a suitable irradiation container and irradiated for some predetermined time. After discharge from the reactor, the irradiated samples are allowed to decay at least 4.5 hours before being chemically processed as described below.

Chemical Processing of Irradiated Samples

Several types of chemical separation schemes may be used to isolate the Pa^{233} radioactivity to free it from all the other radioactive species produced in the irradiation of the sample. The method developed by Moore[11] proved applicable with slight modification to the analyses reported below.

Under normal conditions in the activation analysis method, the desired radioelement is separated from contaminant radioactivities by carrying it through a chemical processing procedure in which a known amount of the natural inactive element is added as an "isotopic carrier" for the induced radionuclide(s) of interest. The same amount of carrier is added to the solutions of both the specimen and the comparator. Losses of the carrier and of the radionuclide in the chemical processing can be compensated for by determining the yield of the separated carrier.

Pa^{233}, while having a convenient half-life for a radiochemical separation, has the disadvantage of not having a stable isotope which can be used as an isotopic carrier. However, Moore[11] has shown that diisobutylcarbinol can be used to separate protactinium quantitatively from other elements by extraction from aqueous solutions of either dilute nitric acid or hydrochloric acid.

In the basic chemical separation procedure considered below, it was assumed, in all instances, that uranium was present in the sample. Since radioniobium (Nb^{95}) is formed in the uranium fission process and will extract in the hydrochloric acid-diisobutylcarbinol system, it was necessary to add oxalic acid to complex the niobium. In those instances where it was felt that serious interferences could be had from the gross amounts of radioactivity induced in the matrix elements or contaminant elements of a sample, it was possible to eliminate these interferences by the use of "scavenging" or holdback carriers in the basic separations procedure. These carriers were usually introduced as solutions of a few milligrams of inactive element(s) into the various steps of the procedure as required. In all the analyses reported, the interferences from other radioelements were negligible.

The Assay of Irradiated Samples

The basic separation procedure used in this work was as follows:

The solid sample was discharged from the quartz ampoule into a platinum dish and equal amounts of concentrated nitric, perchloric, hydrofluoric and sulfuric acids (one milliliter of each) were added. The mixture was digested upon a hot plate at low heat until the sample was completely in solution. Since hydrofluoric acid will interfere in the analysis, additional 1 ml aliquots of sulfuric acid were added to the solution and the solution concentrated at least twice to dense sulfuric acid fumes. In the clay and mud samples, sufficient copper was present to be precipitated as $CuSO_4$. This precipitate could be dissolved by cautiously adding water and gently heating the mixture. After transfer of the solution to a

Table I. Determination of Thorium in Synthetic Mixtures by Neutron Activation Analysis

Solutions		*Ores*	
Thorium taken	*Thorium found*	*Thorium concentration*	*Thorium found*
0.100 μgm (per ml)	0.110 μgm	10.0 μgm	10.0 μgm
	0.095		9.9
	0.100		10.2
	0.105		9.7
	0.100		10.1
	0.100		10.0

60-ml separatory funnel, the solution was treated as in * below.

Aliquots of the aqueous samples were pipetted into a centrifuge tube and evaporated to dryness. The solids were dissolved in 6*N* hydrochloric acid and the solution transferred to a 60-ml separatory funnel. This solution was treated as in * below.

The comparator samples were dissolved in 2*N* nitric acid and diluted to a known volume with additional 2*N* nitric acid. Aliquots from these dilutions were pipetted into a centrifuge tube and processed in the same manner as the aqueous samples.

*A sufficient amount of concentrated HCl and saturated oxalic acid was added to the solution in the separatory funnel to make the solution 6*N* in hydrochloric acid and 4% in oxalic acid.

An equal volume of diisobutylcarbinol equilibrated with 6*N* HCl was added to the mixture and the protactinium extracted by mechanical shaking. (Unless indicated, the time for extraction was for a period of ten minutes.)

After the extraction, the phases were allowed to separate and the aqueous fraction drained off and discarded.

The organic phase was washed twice with a solution of equal volumes of 4% oxalic acid and 6*N* HCl. The washings were accomplished by mechanical shaking. In each instance, after the two phases had separated, the aqueous fraction was drained off and discarded.

An equal volume of 8% oxalic acid was added to the organic fraction and the protactinium extracted by mechanical shaking. After the two phases had separated, the aqueous layer was transferred to a new separatory funnel and the organic layer discarded.

The organic layer was diluted with an equal volume of concentrated hydrochloric acid, and an equal volume of diisobutylcarbinol was added and the extraction repeated.

After the phases had separated, the aqueous layer was drained off and discarded. The organic layer was transferred to a centrifuge tube and the mixture centrifuged at full speed for five minutes.

After the centrifugation, aliquots were pipetted from the organic phase into a suitable container for a radioactivity measurement.

The gamma radioactivity of the samples was determined by means of a gamma scintillation counter having a sodium iodide (thallium activated) crystal. The radiations were further characterized by means of a gamma spectral analysis using a gamma scintillation spectrometer and half-life determinations.

The comparator sample was treated in the same manner as described above. The weight of thorium in the specimen was then calculated as shown in Equation 3. Corrections were made for the volume of diisobutylcarbinol used and the weights of the sample materials.

RESULTS

The synthetic samples used to test the procedure were of two types: (*a*) solutions and (*b*) synthetic ore mixtures. The solutions were prepared from commercially pure thorium nitrate crystals. The ore mixtures were composed of monazite and dunnite. These materials were irradiated and processed by the techniques described above. Typical data obtained in these types of material are given in Table I.

Table II reports on the determination of thorium in dried samples of mud originating from river bottoms. The samples were irradiated and chemically processed as described above.

Similar results were obtained in the assay of a series of clay samples by the same techniques. Typical data obtained in these analyses are reported in Table III.

CONCLUSIONS

From the results reported above, it is felt that the neutron activation analysis method is capable of being a specific, sensitive and precise method of analysis for determining small amounts of thorium in a variety of materials. The limit of detection of thorium by this method is somewhat lower than that obtained by other methods of analysis. This limit is a function of the number of neutrons bombarding the sample, the length of the irradiation period and the efficiency of the counter used in measuring the radioactivity. Most of the results reported below were obtained after a 4-hour irradiation of the samples in a neutron flux of 6×10^{11} neutrons per square centimeter per second. The counting rates obtained in the gamma scintillation counter were of the order of 10^5 gamma

Table II. Determination of Thorium in River Mud by Neutron Activation Analysis

Sample	*Thorium concentration, micrograms/gram*
1	30.6; 28.7; 30.8; 31.9
2	35.3; 30.2; 34.7; 31.3
3	34.2; 32.4; 33.0

Table III. Determination of Thorium in Clay by Neutron Activation Analysis

Sample	*Thorium concentration, micrograms/gram*
1	42.3; 43.1; 40.3
2	63.2; 65.1; 60.8
3	69.3; 71.0; 70.7
4	53.0; 51.4; 47.5

counts per minute per microgram of thorium. Assuming that good statistics for the measurement of the Pa^{233} radioactivity could still be obtained at a counting rate of 10^3 gamma counts per minute, the limit of detection could be minimized at 0.01 microgram of thorium for the same irradiation and analysis conditions. Increased sensitivity can be obtained by irradiating for longer periods of time and at higher neutron fluxes.

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Polarography of Uranium: Polarographic Determination of Uranium in Ores without Preliminary Chemical Separation

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Polarographic investigations of uranium which were done by several authors, using different supporting electrolytes,[1-5] have shown that it is possible to determine uranium by polarographic methods. The uranyl ion is reduced at the mercury electrode to lower oxidation states and at the same time polarographic waves are formed. The process of reduction at the electrode depends on the type of supporting electrolyte and the pH value. Complex-forming and non-complex-forming electrolytes were used in acidic and alkaline medium. Uranium was determined from pure solutions or from mixtures with other elements. The investigations of some new supporting electrolytes, performed in our laboratory,[6] have shown that these electrolytes are very convenient for the determination of uranium alone, or in presence of other elements. The ascorbic acid electrolyte deserves special attention. Its reducing and complex-forming capacities permit the determination of uranium in the presence of a considerable excess of other elements and also in ores, without preliminary separation. Investigations were made with acidic and alkaline ascorbic electrolyte.

EXPERIMENTAL

Apparatus and Reagents

The polarographic measurements were made on the polarograph Radiometer, Copenhagen, type PO3e and Cambridge Polarograph, Pen Recording Type. The pH values of the solutions were measured with a Philips pH-meter GM. The temperature was maintained at the desired level with a thermostat. The fluctuations of the temperature were $\pm$ 0.1°C. A saturated calomel electrode (SCE) was used as reference electrode. In the greater part of the experiments, the polarization rate of the dropping electrode was 0.1 v per 17.4 sec, and the time of dropping was about 3 seconds. We used distilled and anodically purified mercury. The standard solutions of uranium were made from U_3O_8, obtained from uranium solutions purified by ether extraction. The purity of ascorbic acid was according to "Merck" standards; other reagents used were either "Merck" or "pro analysis".

The diffusion current was measured and corrected for the residual current.

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Quality of Uranium Wave as a Function of pH

The polarographic behaviour of uranium and the elements accompanying uranium in ores was described previously.[7] The ascorbic electrolyte was used and the dependence on pH values given. We have also described a method for the direct determination of uranium in ores.[8] This report deals with detailed investigations of the polarographic determination of uranium in ores, using an acidic or alkaline ascorbic supporting electrolyte, and with the reduction of the uranyl-ascorbic complex on the dropping electrode.

Studying the uranium waves in the pH range from 1 to 9.5, it was found that at pH < 2, waves possess a certain residual current (for a uranium concentration $< 1 \times 10^{-5}$ gm/ml). An increase of pH produces a decrease of the residual current which disappears at pH > 3.5. The residual current at low pH values is caused by the presence of traces of oxygen which can not be completely removed with nitrogen. At pH > 3.5 it is not necessary to remove oxygen with inert gases, since the supporting electrolyte itself reacts quantitatively with oxygen. This permits the formation of excellent uranium waves at pH > 3.5.

By measuring the diffusion current at different pH and known concentrations of uranium, it was found that $i_d/C = K$ at pH = 1–9.5. This shows that uranium can be determined in acidic as well as in alkaline ascorbic supporting electrolyte. Because of the complete absence of oxygen, one obtains well formed waves for the uranium concentration of 2×10^{-6} gm/ml, which is the maximum sensitivity of Cambridge Polarograph.

The change of half-wave potential of uranyl ion in the ascorbic supporting electrolyte as a function of pH,[7] shows that for the same concentration of supporting electrolyte, a change of pH brings about a change of the composition of the complex. This can be seen by observing the colours of the complex in acidic and alkaline media.

The Analysis of Waves. Reversibility of Electrode Reaction 1,2

By the analysis of the anodic-cathodic wave of the mixture U(VI) and U(V)-complex, that of the cathodic wave of the uranyl ion complex, and by other methods, it was found that the reduction

of the uranyl-ascorbic complex to U(V), at the dropping mercury electrode, is reversible. This was established by the following experiments:

A cell which can be used for electrolysis and polarographic investigations was made in a shape somewhat different from that used by Kraus and collaborators.[9,10,11] The volume of the cell was 10–20 ml. Instead of mercury we used platinum as the anode, while the cathode was made of a tungsten plate. The anodic and cathodic space are separated by saturated KCl-agar gel electrolytic bridge. The end of the bridge is somewhat wide and serves as the anodic space. On the side, the bridge is connected to the cell, and when the polarogram is being recorded, the saturated calomel electrode is connected to it. The dropping electrode is dipped into the cell, and the mercury which drops from it falls into a draining-off side tube, and so leaves the cell.

Uranium(VI), in 0.1–0.005*N* chloride or sulphate solution (pH 2.7–3) is placed in such a vessel. The solution is electrolysed with 3–5 ma and —0.5 to —0.6 v cathode potential vs SCE. When enough U(V) is produced, the electrolysis is stopped and the polarographic circuit switched on. An anodic-cathodic wave is obtained, which shows the reversibility of the reduction and oxidation of U(VI) and U(V) in chloride and sulphate solutions. Ascorbic acid is now placed in this solution which then shows the characteristic colour of the uranium-ascorbic complex. The polarogram obtained shows the anodic-cathodic wave of the redox process of the U(VI) $\rightleftarrows$ U(V)-complexes. During the whole experiment the solution is isolated from air by the use of nitrogen.

The resulting anodic-cathodic wave has the same half-wave potential. The plotted values of E, i, $(i_d)_a$, $(i_d)_c$ show that the relation between E and $\log [i - (i_d)_a]/[(i_d)_c - i]$ is given by a straight line with the slope equal to 0.0603 v. E is the potential of the dropping electrode, i is diffusion current at the potential E, $(i_d)_a$ is the anodic diffusion current, $(i_d)_c$ is the cathodic diffusion current. The ratio $E/\log[i/(i_d - i)]$ for the cathodic wave has the slope value equal to 0.061 v.

According to Tomes[12] the reversible processes are those which have the potential difference $E_{3/4} - E_{1/4}$ of dropping electrode equal to —0.056 v. The currents corresponding to these potentials are $3i_d/4$ and $i_d/4$, respectively. When these considerations were applied to the cathodic wave of the uranyl-ascorbic complex, it was found that $E_{3/4} - E_{1/4} =$ —0.0564 v. The measurements of $E_{3/4} - E_{1/4}$ at different temperatures (18°, 25°, 29°C) gave values close to —0.056 v. The formation of an anodic-cathodic wave of the mixture U(VI)- and U(V)-complex, the values

$$E/\log \frac{i - (i_d)_a}{(i_d)_c - i},\quad E/\log \frac{i}{i_d - i}$$

and

$$E_{3/4} - E_{1/4}$$

all show that the electrode process is reversible and that only one electron is exchanged.

Since the half-wave potential of the uranyl ion complex depends on the dissociation constant of the complex, we measured the shift of half-wave potential as a function of the concentration of ascorbic ions. From the experimental data and the equation

$$\frac{\Delta E_{1/2}}{\Delta \log C_x} = -\left(\frac{p-q}{a}\right) 0.0591 \qquad (1)$$

we determined the difference of coordination numbers, $p - q$, of the U(VI)- and U(V)-complexes. The curve showing the experimental values of $E_{1/2}$ as a function of $\log C_x$, C_x = the concentration of ascorbic ions, is a straight line with a slope equal to 0.056 v, so that Equation 1 becomes

$$-0.056 = -\left(\frac{p-q}{a}\right) 0.0591$$

From this we concluded that $p - q$ is very close to unity, since it was shown earlier that $a = 1$.

The pK of ascorbic acid at 25°C, and the ionic strength $\mu = 0.2$ is, according to the measurements of Gal,[13] equal to 4.06. For that reason the measurements of the shift of the half-wave potential as a function of the concentration of ascorbic acid were done at pH = 4.06, ionic strength $\mu = 0.2$ and 25°C. The experiments were performed in the following way:

The uranium waves were first obtained in 0.2*M* $NaClO_4$, and then the concentration of perchlorate decreased, while that of ascorbinate was increased, taking care that pH = 4.06, $\mu = 0.2$ and the temperature kept at 25°C. The polarisation rate of the dropping electrode is 0.03 v/17.4 sec, or, in other words, 1 cm of radiometer polarographic paper corresponds to 0.03 v. The measurements of $E_{1/2}$ and C_x, under the above mentioned conditions, gives the following results (see Table I).

The reduction of the simple uranyl ion at the dropping electrode can be represented by the following equation

$$M^{n+} + a \cdot e \rightleftarrows M^{(n-a)+} \qquad (2)$$

while the reduction of the complex uranyl ion is given by

$$MX_p^{(n-pb)+} + a \cdot e \rightleftarrows MX_q^{(n-a-qb)+} + (p-q)X^{-b} \qquad (3)$$

M denoting the uranyl, and X the ascorbic ion.

By subtracting the first equation from the second, one obtains the final equations of the reversible electrode process:

$$MX_p^{(n-pb)+} + {}^{(n-a)+} \rightleftarrows MX_q^{(n-a-qb)+} + M^{n+} + (p-q)X^{-b} \qquad (4)$$

The normal potential of the redox process of U(VI) $\rightleftarrows$ U(V)-complex in ascorbic solution, at pH 4.06, was determined from the shift of half-wave potentials of the uranyl complex, for different concentrations of ascorbate, C_x, and from the half-wave potential of the simple uranyl ion in a perchlorate

Table I

					Average
$(E_{1/2})_c$	−0.204	−0.264	−0.288	−0.307	
log C_x	−2.602	−1.5228	−1.00	−0.6989	
$\Delta E_{1/2}$	0.06	0.085	0.1035	0.018	
$\Delta \log C_x$	−1.08	−1.60	−1.90	−0.301	
$\frac{\Delta E_{1/2}}{\Delta \log C_x}$	0.056	0.053	0.054	0.06	0.0558
$\frac{p-q}{a}$	0.95	0.89	0.92	1.01	0.94
E_c^0	−0.12	−0.115	−0.108	−0.109	−0.11 ± 9%
E^0	−0.17	−0.165	−0.158	−0.159	−0.16 ± 4%
$\frac{K_{ox}}{(K_{red} = K)} \times 10^3$	1.47	1.78	2.27	2.20	1.93 ± 24%

solution. The experimental values of $(E_{1/2})_c$, $(E_{1/2})_s$ and C_x, where c denotes the complexing and s the simple ion, taken into the equation

$$(E_{1/2})_c - (E_{1/2})_s = E_c^0 - E_s^0 - \left(\frac{p-q}{a}\right) 0.0591 \log C_x \quad (5)$$

give the value of E_c^0, in the ascorbic solution of pH = 4.06.

C_x is calculated from the pK value of the dissociation constant, at pH = 4.06. E_s^0 is the normal potential of the redox system $UO_2^{++} \rightleftarrows UO_2^+$, and according to Latimer[14] has the value of 0.05 v vs NHE. Since $(p-q)/a$ is unity, Equation 5 becomes

$$(E_{1/2})_c - (E_{1/2})_s = E_c^0 - E_s^0 - 0.0591 \log C_x \quad (6)$$

E_c^0 was determined for several values of C_x, as can be seen from Table I. The standard electromotive force and the equilibrium constant of reaction (4) were determined from the experimental data. The equilibrium constant is

$$K = \frac{[MX_q^{(n-a-qb)+}][M^{n+}][X^{-b}]^{p-b}}{[MX_p^{(n-pb)+}][M^{(n-a)+}]} = \frac{K_{ox}}{K_{red}} \quad (7)$$

while the electromotive force E^0 is

$$E^0 = E_c^0 - E_s^0 = \frac{RT}{aF} \ln K = \frac{RT}{aF} \ln \frac{K_{ox}}{K_{red}} \quad (8)$$

By subtracting the wave equations of the simple and complex ion, one obtains

$$(E_{1/2})_c - (E_{1/2})_s = E_c^0 - E_s^0 - \left(\frac{p-q}{a}\right) 0.0591 \log C_x \quad (9)$$

or

$$(E_{1/2})_c - (E_{1/2})_s = 0.0591 \log \frac{K_{ox}}{K_{red}} - \left(\frac{p-q}{a}\right) \times 0.0591 \log C_x \quad (10)$$

$(E_{1/2})_s$ is the half-wave potential in the perchlorate electrolyte under the same conditions as in the ascorbic electrolyte. The measured values of E^0 and K are given in Table I. K_{ox} and K_{red} are the dissociation constants of the complexes U(VI) and U(V).

It was shown above that $i_d/C = k$, and that it does not depend on pH, so that one can conclude that the uranyl complex is reduced in the same manner in an alkaline as it is in an acid medium.

The investigation of the electrode reaction and the reduction of the uranyl complex in a phthalate and benzoate supporting electrolyte, described earlier,[6] have proved that the reduction is reversible to U(V). Anodic-cathodic waves with the same half-wave potentials were obtained in both cases. The analysis of the cathodic waves gives the values for $E/\log [i/(i_d - i)]$ equal to 0.0583 v in the benzoate, and 0.062 v in the phthalate supporting electrolyte.

The benzoate complex[15] is reduced according to the equation

$$UO_2(C_6H_5CO_2)_3^- + e \rightleftarrows UO_2(C_6H_5CO_2)_2^{--} + C_6H_5CO_2^- \quad (11)$$

with a preliminary dissociation

$$UO_2(C_6H_5CO_2)_3^- \rightleftarrows UO_2^{++} + 3C_6H_5CO_2^- \quad (12)$$

One can expect that the phthalate complex is reduced in the same manner.

The waves of the oxidation states lower than UO_2^{2+} were not examined quantitatively, but it was established that it is possible to obtain a weakly formed wave which corresponds to the reduction U(V) → U(III), with the diffusion current twice as great as for the first wave.

The presence of gelatine influences the height of waves as well as the half-wave potential. Because of the specific action of the gelatine on the half-wave potential of different ions it is possible to separate the uranium waves from those of other elements.[7]

The Determination of Uranium in the Presence of Other Elements in the Ascorbic Supporting Electrolyte

Not one of the electrolytes known so far has better characteristics than the ascorbic electrolyte. It not only forms complexes but also reduces all ions more positive than 0.5 v vs hydrogen, to lower valency states. In earlier reports we have described the determination of uranium in presence of other elements in ascorbic supporting electrolyte,[6] and, accordingly, the determination of uranium in ores.[8] We have also described the chemical and polarographic behaviour of elements in that electrolyte, in the pH range 1–9.5.[7] However, in the earlier determination of uranium in mixtures of elements, the

concentration of each ion present was not more than three times greater than the uranium concentration. For that reason we have determined the limiting concentration of the elements accompanying uranium, in which uranium can be determined qualitatively and quantitatively. This was made for each kind of ion separately, depending on pH, in an acid medium. It turned out that, at pH > 1.5, Pb and Tl interfere with the uranium wave, while at pH < 1.5 the interference exists only if the concentrations are a hundred times greater than the concentration of uranium. Telurium and tin cause interferences at all pH values by masking the uranium waves. A smaller interference exists for the majority of elements at pH = 3–5. In this pH range, uranium can be determined in the presence of a great excess of other elements, as can be seen from Table II.

The results refer to the acidic ascorbic solution. The concentrations of uranium were $< 10^{-5}$ gm/ml.

Mixtures were made consisting of uranium and one ion of all the elements investigated, and the uranium determined quantitatively by using the data given in Table II. Measurements were made in 0.5*N* ascorbic solution, with 0.001–0.01% of gelatine and at pH = 3–5. The results are within the limits of error, as can be seen in Table III. The separate mixtures of uranium with Pb, Tl, Te, Se, Sn^{4+}, Sn^{2+}, Sb and Mo were not quantitatively analysed, but their presence was determined by the use of data in Table II. Platinum is reduced at a more positive potential than uranium.

In addition to these separate measurements we have determined uranium in the presence of all elements whose waves do not interfere with uranium waves. The results are given in Table IV. The concentration of uranium in the analysed mixture was 3×10^{-5} gm/ml.

The interferences caused by Te, Pb, Tl, Sb (pH 3–5), at greater concentrations than allowed by the data in Table II, can be easily cancelled by passing the solution through the cadmium reductor.[6] This eliminates all ions more positive than Cd^{2+}. The ions of Pb, Tl, Sb, Bi and Te are reduced to their elements by ascorbic acid if Pd^{2+} ion is present in the solution. Thus, these ions can be eliminated from the solution by adding a solution of Pd, either directly into the polarographic cell or into the sample prepared for the analysis, and then ascorbic acid added. This process is slowed down by gelatine which should, for that reason, be added after palladium. The amount of Pd should be 2–3 times greater than the concentration of these elements.[16] In that way, the interference of these elements is eliminated. Usually, 0.5*M* ascorbic acid is used, but satisfactory results can also be obtained with 0.05*M* acid, if the solution does not contain a great amount of admixtures.

The anions Cl^-, SO_4^{--}, NO_3^- do not cause any interference, while greater amounts of phosphate diminish the uranium wave.

Determination of Uranium in the Alkaline Ascorbic Electrolyte

The polarographic determination of uranium is rarely carried out in alkaline electrolytes. In the carbonate electrolyte, ammonium and sodium carbonate are used in most cases.[2,3] The experiments have shown that excellent uranium waves can be obtained from an alkaline solution of ascorbic acid. The diffusion current of these waves is a linear function of the concentration of the uranyl ion. The waves have no maxima and the solution contains no oxygen, so that well formed waves are obtained at the maximum sensitivity of the Cambridge Polarograph, for the concentration of 2×10^{-6} gm/ml. Uranyl ion is reduced to the pentavalent state. The half-wave potentials of uranium and other elements, as a function of pH, were given earlier.[7] We have not given the half-wave potentials for those ions which were reduced to the elementary state in an acid medium. The reduction of these elements in alkaline media was not investigated. The procedure was to add a solution of the elements to an acidic ascorbic solution, and then increase the pH by adding ammonia. If selenium is placed in the alkaline ascorbate, it will not be reduced to the element, as it is in the acidic medium, but gives waves at about

Table II

Ion	*pH*	*Ratio of ion/uranium concentration*	*Ion*	*pH*	*Ratio of ion/uranium concentration*
Pb^{2+}	< 1.5	100	Ti^{3+}	< 1.5	100
Cd^{2+}	3–5	700	Bi^{3+}	1–5	10
Cr^{3+}	2–5.5	800	Cu^{2+}	1–6	10
Pd^{2+}	1–4	200	Th^{4+}	1–6	400
Ag^{+}	1–4	400	Zn^{2+}	2–5	800
Hg^{2+}	3–5.5	200	Co^{2+}	1–6	900
Au^{3+}	1–4	200	Mn^{2+}	1–5.5	800
Se(IV)	1–4	100	As^{3+}	1–5.5	600
Ni^{2+}	1–6	700	Ti^{4+}	2–6	600
Sn^{4+}	2–4.5	500	V(V)	< 1; 2–4; > 7	100; 3; 400
Sn^{2+}	*	*	Mo(VI)	2–4	3
Fe^{3+}	1–4	600	Te(IV)	*	*
W(VI)	3–5	100	Sb^{3+}	3–6	3

* Interferes.

Table III

Element added to U	Mn	Fe	Co	Ni	Cd	n	Cr	Ag	Au	Hg	Bi	Ti	V	Th	W	As	Pd	Cu
U given gm/ml $\times 10^{-5}$	1.0	1.96	1.98	1.0	1.0	1.0	1.0	1.0	1.98	0.97	1.0	1.62	1.25	0.96	1.0	1.0	0.98	1.0
Element added gm/ml $\times 10^{-3}$	4.0	1.96	3.96	4.0	4.0	2.0	4.0	1.0	1.98	.097	0.1	4.86	0.05	0.48	0.4	4.0	0.49	0.08
Element/U ratio	400	100	200	400	400	200	400	100	100	100	10	300	4	50	40	400	50	8
U found %	98.04	100.4	98.58	99.84	98.04	98.46	96.34	101.4	100.4	104.5	98.2	98.58	107.2	96.6	100.3	101.6	99.85	98.04

Table IV

Solution contains	Zn	Ti	Ni	Sn	Mn	Cd	As	Fe	Hg	Ag	Se	W	Au	Th	Cr	Co	Bi	Pd	Cu	Pt	I	Zn	U found %
Element/U concentration ratio	10	10	10	10	10	10	10	10	10	10	10	10	10	5	10	10	1	10	1	3	1	170	97.7

—0.9 v vs SCE. As soon as the solution becomes acidic, reduction takes place and selenium is precipitated. Interferences with the uranium wave can be caused only by elements whose waves coincide with those of uranium.[7] In an alkaline medium, high concentrations of molybdenum and vanadium do not interfere.

From alkaline solutions of phthalates and benzoates, uranium is precipitated as hydroxide.

It is not necessary to bubble the solution of the ascorbic electrolyte with nitrogen to remove oxygen, at pH > 3.5. The efficacy of ascorbic solution in absorbing oxygen increases with pH.

The Determination of Uranium in Ores, Using an Acidic Ascorbic Solution

The above results were applied to the direct polarographic determination of uranium in ores. If the ore contains weakly soluble sulphates, the precipitates of which are crystalline, there is no interference with the determination of uranium. When analysing the ore, it is necessary, in most cases, to add more gelatine, especially in the case of low grade ores. If the ore contains interfering elements, they can be eliminated with a palladium or cadmium reductor. The presence of vanadium and molybdenum in a greater proportion than allowed by Table II, in acidic medium, increases the positive error for uranium.

A considerable number of ores of different composition were analysed in the above manner. The results were compared with those obtained by other methods: colorimetric, fluorimetric and radiochemical. They are given in Table V.

As can be seen from the table, the agreement between the different methods is good.

The analysis of some samples has shown that they contain less than 50 gm/total of uranium, which was confirmed by fluorimetric analyses. Some ores containing enough V and Mo were precipitated with ammonia and the U determined in the precipitate.

Table V

Ore	Polarographic method gm U/Total	Colorimetric method gm U/Total	Fluorimetric method gm U/Total	Radiochemical method gm U/Total
1	1006		1020	970
2	345	338	346	325
3	300	292	294	
4	120	125	128	123
5	194	191	196	
6	156		150	
7	168		172	
8	395			

The Determination of Uranium in Ores with the Use of Alkaline Ascorbic Electrolyte

An alkaline ascorbic electrolyte was used to determine uranium in carbonate solutions of ores. The finely powdered ore was mixed with a solution of sodium carbonate and stirred for 3 hours in an autoclave[17] at 115°C, at the pressure of 1.7 atm. The solution of sodium carbonate contained 12–65 gm of Na_2CO_3 per liter. The solution is separated from the precipitate by decanting or filtrating. Since the ores in most cases contain organic materials which pass into carbonate solution and interfere with the determination of uranium, they had to be destroyed with nitric and sulphuric acid. The procedure consists in evaporation to dryness of the carbonate solution with nitric and sulphuric acid. The dry residue of sulphate is dissolved in water, ascorbic acid added followed by ammonia until the medium is alkaline. The solution is then put into a normal bottle from which the samples are taken for analysis. Excellent uranium waves, without interference, were obtained. It was not necessary to bubble the solution with nitrogen nor to add gelatine to it. The carbonate solutions of ores contain a smaller number of

admixtures and in smaller concentration than the acidic solutions, since many elements are not dissolved in carbonates. For that reason the polarographic waves of ores in alkaline solutions are often better than those in acidic solutions. This method is especially convenient for checking the carbonate dissolution of uranium ores rich in Mo and V, on an industrial scale. The uranium content of the carbonate solution often does not correspond to the real content of uranium in the ore because the dissolving is not quantitative. Table VI shows the results of analyses of carbonate solutions of several different ores.

Table VI

Ore	*1*	*2*	*3*	*4*	*5*	*6*
mg of U/100 ml of solution	5.72	1.89	1.62	2.61	1.01	1.60

The procedure where the ore is melted with alkali carbonates, the melted mixture dissolved and filtrated, and uranium determined in the filtrate by the use of alkaline ascorbic electrolyte, in most cases gives values lower than the real content of uranium. The reason for it is the absorption of uranium on the precipitated hydroxides of the elements present.

CONCLUSION

A detailed investigation of uranium and other elements in acidic and alkaline ascorbic supporting electrolyte was made. It was found that i_d of the uranyl ion does not depend on pH, and that i_d/C is equal to k in acidic and alkaline medium. The dependence of the wave quality on pH was shown. The ascorbic supporting electrolyte absorbs oxygen from the solution at pH > 3.5 and gives well formed waves in low concentrations of uranium to 2×10^{-6} gm/ml.

The study of the electrode reaction has shown that the reduction of U(VI) $\rightleftarrows$ U(V)-complex is reversible and that only one electron is exchanged. The anodic-cathodic wave of the mixture U(VI) and U(V) in acidic ascorbic solutions was obtained. The relations for the anodic–cathodic and for the cathodic waves are

$$E/\log \frac{i - (i_d)_a}{(i_d)_c - i} = 0.0603 \text{ v}$$

and

$$E/\log \frac{i}{i_d - i} = 0.061 \text{ v}$$

respectively. $E_{3/4} - E_{1/4}$ is equal to -0.0564 v and does not depend appreciably on the temperature. It was found that the normal potential E_c^0 of the system U(VI) $\rightleftarrows$ U(V) in the ascorbic solution, at pH 4.06 and 25°C, is equal to -0.11 v vs NHE, and the standard electromotive force E^0 of reaction 4, equal to -0.16 v vs NHE. The equilibrium constant for reaction 4 was determined as well as the ratio of the dissociation constants of U(VI)- and U(V)-complexes. The difference of the coordination numbers of these complexes, $p - q$, was also determined. All these measurements, given in Table I, were made at pH = 4.06, ionic strength $\mu = 0.2$ and 25°C.

We have established the limiting concentration of the elements accompanying uranium, which permit the determination of uranium in an acidic medium. The quantitative determination of uranium in the presence of a great excess of other elements was performed. It was demonstrated that uranium can also be determined in an alkaline ascorbic supporting electrolyte. A method was given for the polarographic determination of uranium in ores, in acidic or alkaline medium, without separation, and the procedure for the elimination of interferences described. Analyses of a number of ores in an acidic solution were made as well as those of carbonate solutions of ores in an alkaline solution.

ACKNOWLEDGEMENT

The author is indebted to Professor P. Savić for the interest and help during this work.

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Application of the Polarographic Technique to the Determination of Tin in Uranium Compounds

By C. Sambucetti, E. Witt and A. Gori,* Argentina

Tin can be determined polarographically in various electrolytes, according to its valence state and the type of material to be analyzed.

The complex chlorostannate ion $(SnCl_6)^=$, if present in solutions containing a high concentration of H^+ and Cl^- ions, produces a very well-developed double wave (Fig. 1); the first part of the wave corresponds to the reduction of the $(SnCl_6)$ ion to $(SnCl_4)^-$, and the second part to the reduction to metallic tin.[1]

The development of this wave is greatly affected by the concentrations of the H^+ and Cl^- ions, since complex chlorine ions of higher order are formed as the concentrations of these two ions increase, until finally $(SnCl_6)^=$ predominates.

The H^+ concentration should not be too high, or else the plateau of the diffusion current becomes excessively steep.

Optimum conditions are obtained by employing a base electrolyte of 4*M* NH_4Cl and 1.5*M* HCl, containing 0.005% of gelatine.[2, 5]

In the method we have developed, a double separation is required to separate the tin from interfering elements: in the first state, it is separate from uranium by extraction of its cupferrate with chloroform; in the second, aluminum is used as a carrier, and the tin is precipitated as the hydroxide, the residue being analyzed polarographically.

MATERIALS AND APPARATUS

The materials used were those of ordinary analytic use. The separation of the hydroxides precipitate is performed by centrifuging; the final readings are made on a Tinsley polarograph.

REAGENTS

Reagents were: sulfuric acid, pure for analysis (sp.gr. 1.84); nitric acid, pure for analysis (sp.gr. 1.40); hydrochloric acid, pure for analysis; perchloric acid, pure for analysis (sp.gr. 1.67); ammonia, pure for analysis (sp.gr. 0.91); sulfuric acid solution, 10%; potassium permanganate solution, 1%; cupferron solution, 6%; pure chloroform; aluminum chloride solution (2 mg/ml); ammonium chloride solution, 4*N*; gelatine solution, 1%; and standard solution of tin.

Pure $SnCl_2 \cdot 2H_2O$ was used; 2400 gm are treated with 50 ml of concentrated HCl, heating to dissolve it; the volume is raised to 250 ml with 1:1 HCl. The actual concentration is determined by gravimetric analysis. This solution should be prepared fresh each week. Two others, prepared from it by suitable dilution, contain 0.05 and 0.25 gm Sn per liter.

PROCEDURE

The characteristics of the polarographic wave of the chlorostannate ion make it possible to detect tin concentrations of the order of magnitude of 10^{-6}. The range of concentrations over which we applied the method runs from 2 to 100 γ/ml.

The sample is dissolved in the most convenient manner, then treated with sulfuric acid and brought to the fuming point, and diluted to 100 ml so that the amount of acid is 8–10% by volume.

Separation of the Tin

The acid solution obtained is raised to the boiling point, and the uranium is oxidized with 1% $KMnO_4$ solution. It is then cooled down to about 5°C and transferred to a separatory funnel. There it is treated with 6% cupferron in 5 ml portions and shaken and extracted with chloroform until a new portion of cupferron produces a white precipitate and the chloroform solution is colorless. All solutions should be at about 5°C.[3]

5 ml of nitric acid and 1 ml of sulfuric acid are added to the chloroform extracts and carefully heated over a sand bath to drive off the chloroform. The organic matter is destroyed by heating with sulfuric and perchloric acids to the point where white fumes are given off.

Once this has been done, it is allowed to cool and the solution is transferred to a centrifuge tube (25 ml capacity), in which the tin is precipitated.

Precipitation of the Tin with Aluminum as Carrier

The solution resulting from the destruction of the organic matter contains, in addition to the tin, other elements that must be eliminated, since they may interfere with the final determination.[4]

To this end, the solution is diluted down to some 5 or 8 ml, 1 ml of 0.2% aluminum solution is added, with a drop of methyl red, and it is neutralized with ammonia until the indicator changes color, adding 0.2 ml in excess. Too great an excess of ammonia should be avoided. This is left to digest for a few

Original language: Spanish.
* National Atomic Energy Commission.

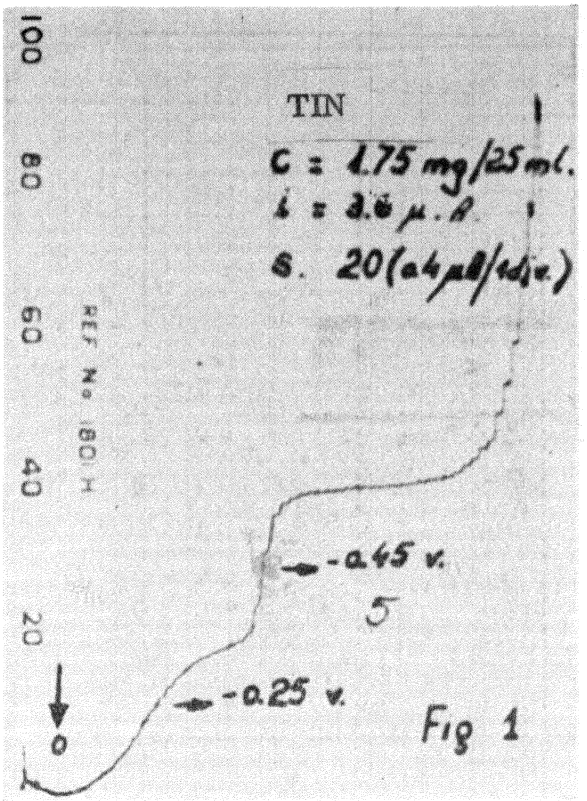


Figure 1

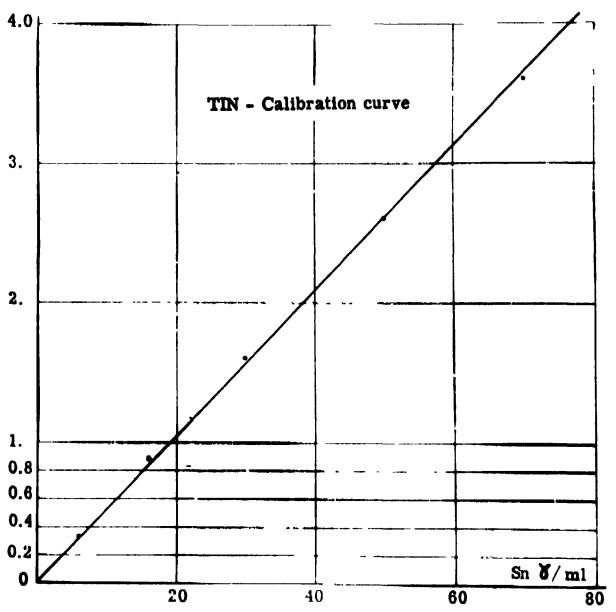


Figure 2

minutes on a water bath. The aluminum precipitate that acts as carrier of the tin is centrifuged for some 20 minutes at the maximum speed of the centrifuge. Under these conditions, the precipitate remains perfectly adherent to the walls of the bottom of the tube, and may be decanted easily.

Polarographic Determination

The precipitate of hydroxides is dissolved in 5 ml of HCl and, as it may contain varying amounts of iron which accompanies the tin throughout the process, hydroxylamine hydrochloride is added, after which it is boiled for about 10 minutes. It is then transferred to a 25-ml flask; the walls of the tube are washed well with 4*M* NH_4Cl, 1 ml of 1% gelatine solution is added, and the volume is made up with 4*M* NH_4Cl solution. The polarograms are made with fractions of this solution, passing nitrogen through 5 minutes before each determination.

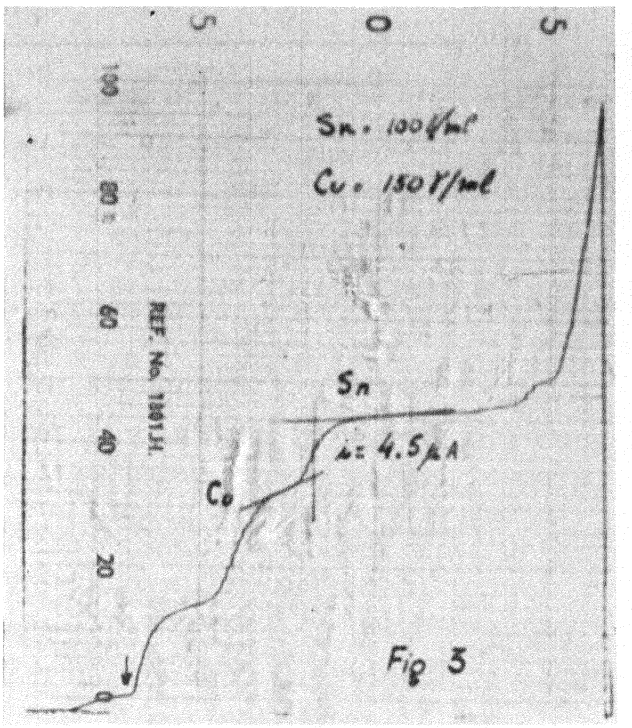


Figure 3

EXPERIMENTAL

Polarogram of Tin

Figure 1 shows the two waves of tin; under working conditions the approximate half-wave potentials are −0.25 and −0.45 volts. The second wave is the one used to determine the tin concentration.

The dropping electrode employed had a dropping time of 4 seconds; height of the mercury column 50 cm, temperature 25°C.

Calibration Curve

Solutions containing amounts of tin between 0.15 and 1.75 mg were put into centrifuge tubes and precipitated; this was followed by centrifuging and polarographic analysis in the manner indicated.

The results are given in Table I and Fig. 2.

Table I

	Total tin		*Intensity*
	mg/25 ml	*γ/ml*	*μa*
1	0.150	6	0.3
2	0.400	16	0.9
3	0.750	30	1.6
4	1.250	50	2.6
5	1.750	70	3.6

Table II

Element	*Extraction with cupferron*	*Precipitation with ammonia*	*Polarography*	*Interference with the method*
Copper	Partially extracted	Absorbed	Troublesome in large amounts	Does not interfere
Bismuth	Extracted	Part. precip.	Troublesome in large amounts	Does not interfere
Antimony	Not extracted	Part. precip.	Troublesome in large amounts	Does not interfere
Lead	Not extracted	Part. precip.	Interferes	Does not interfere
Iron	Extracted	Precip.	Troublesome in large amounts	Interferes
Zirconium	Extracted	Precip.	Not troublesome	Does not interfere
Vanadium	Extracted	Absorbed	Troublesome in large amounts	Does not interfere
Titanium	Extracted	Precip.	Not troublesome	Does not interfere
Molybdenum	Extracted	Absorbed	Troublesome in large amounts	Does not interfere
Niobium	Extracted	Precip.	Does not interfere	Does not interfere
Tungsten	Extracted	Absorbed	Does not interfere	Does not interfere
Tantalum	Extracted	Precip.	Does not interfere	Does not interfere

Checking the Method

Uranium was purified by ether extraction of the nitrate and subsequent precipitation as the peroxide.

To samples containing 1 gm of U there were added increasing amounts of tin, followed by extraction with cupferron, destruction of the organic matter, precipitation of the hydroxides, centrifuging, and the final polarographic determination.

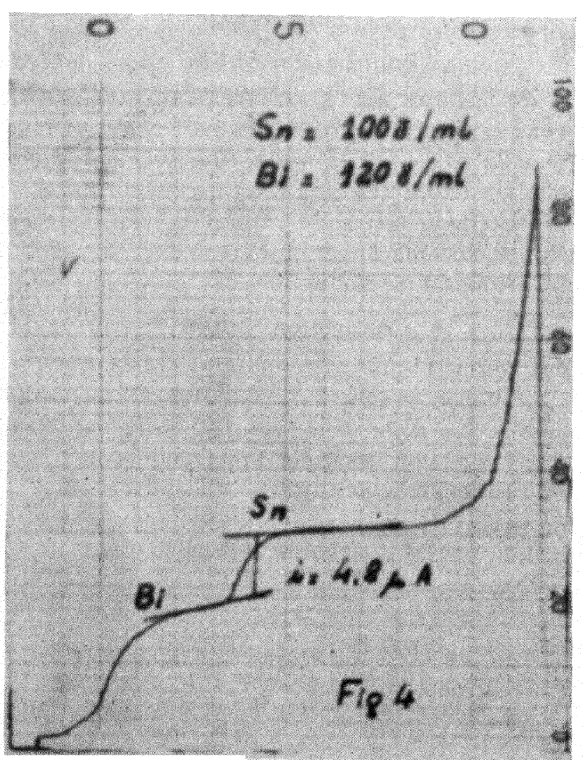


Figure 4

RESULTS

Sn added γ/ml	*Intensity μa*	*Sn recovered γ/ml*
30	1.6	30
20	1.00	19
8	0.4	7.6

Interferences

The following elements were considered:

Copper gives a wave with an approximate potential of — 0.2 volts in the medium studied, so that if it is present in great excess, it practically prevents reading of the tin wave (Fig. 3).

Bismuth produces a wave at — 0.23 volts: like copper, it does not interfere unless its concentration is much greater than that of the tin (Fig. 4).

Lead yields a wave that has the same potential as tin and adds on to the wave of the latter; hence, tin can not be determined in the presence of lead (Fig. 5).

Iron interferes only if present in great excess, since the wave it produces in this medium appears at — 0.05 volts (Fig. 6).

Zirconium does not interfere in this medium (Fig. 7).

Titanium does not exhibit a wave in the medium studied (Fig. 8).

Niobium does not interfere in the polarography of tin (Fig. 9).

Antimony exhibits a wave at approximately — 0.2 volts, so that it is only troublesome if present in large amounts (Fig. 10).

Molybdenum is troublesome only in large amounts, since the molybdate ion exhibits a wave at about — 0.2 volts (Fig. 11).

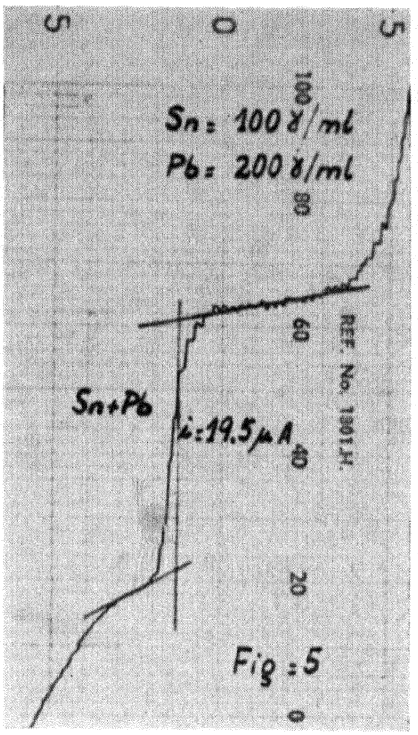
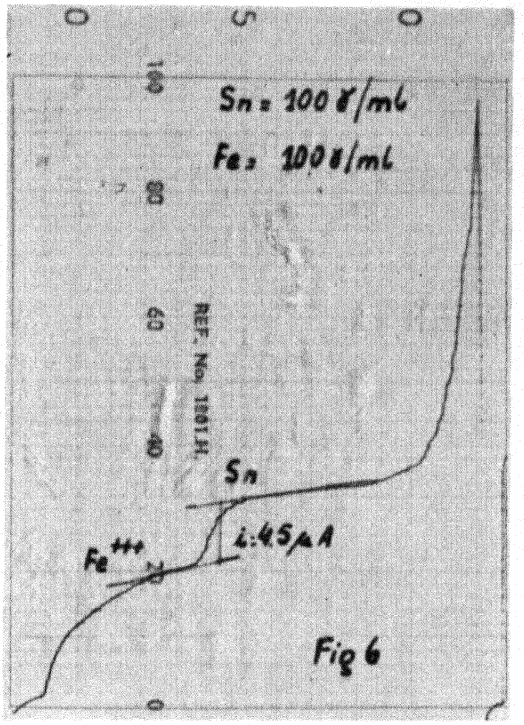


Figure 5



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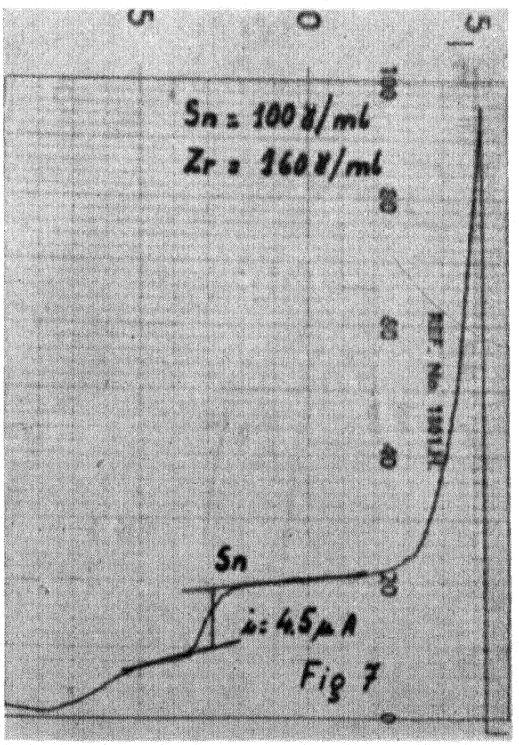
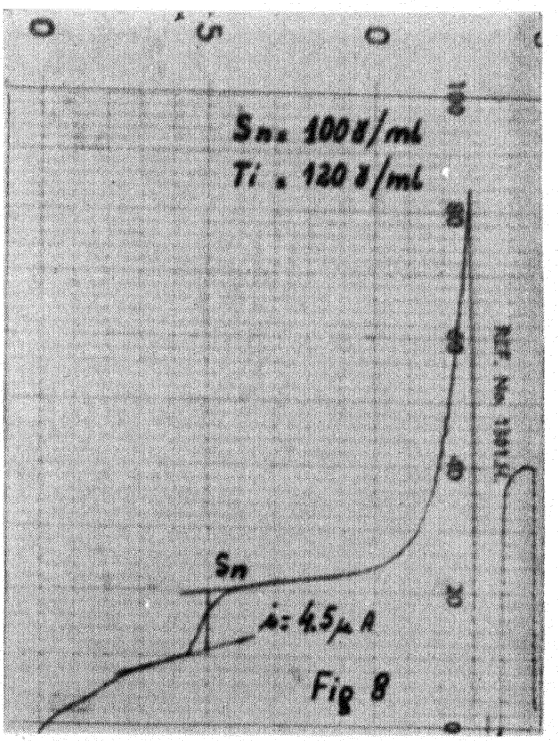


Figure 7



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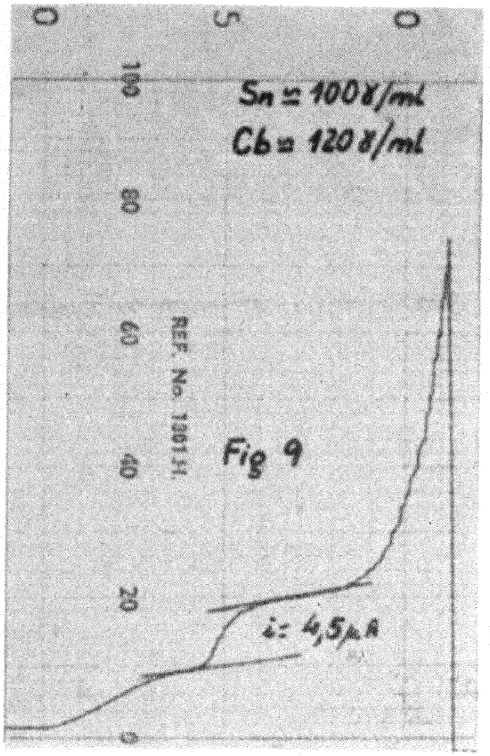

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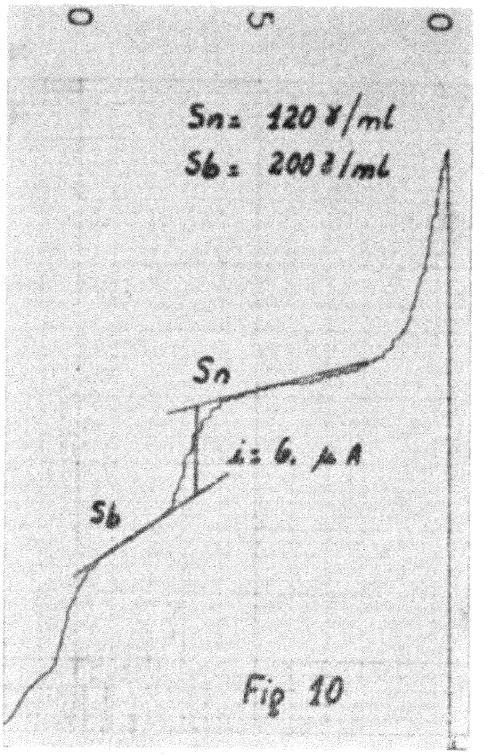

Figure 10

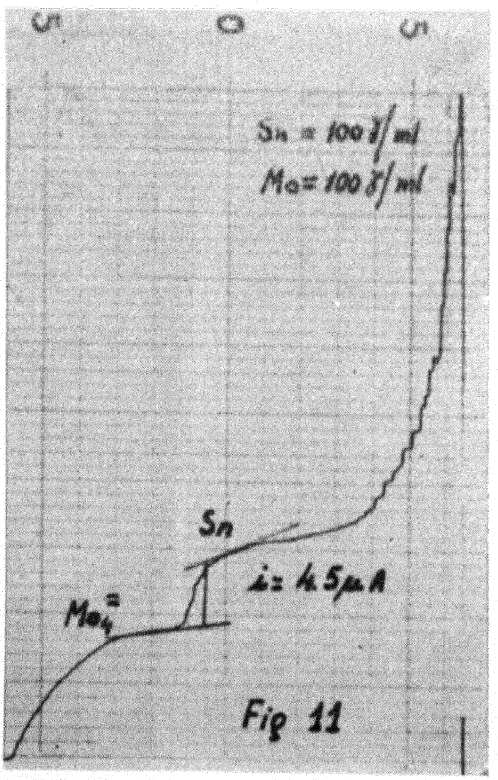

Figure 11

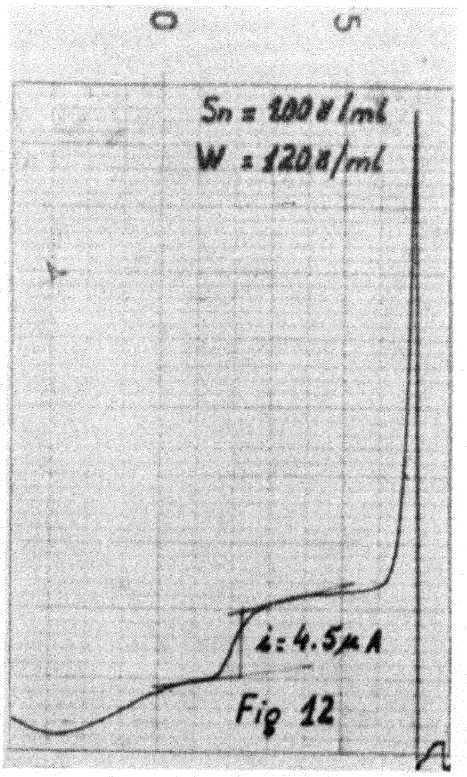

Figure 12

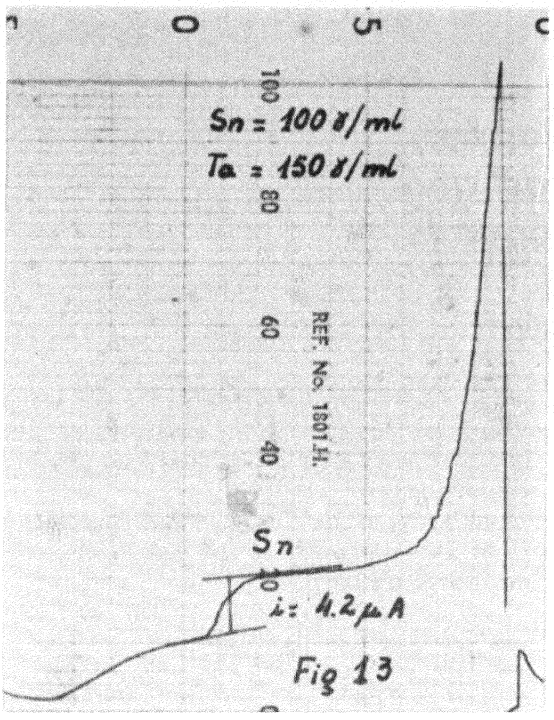

Figure 13

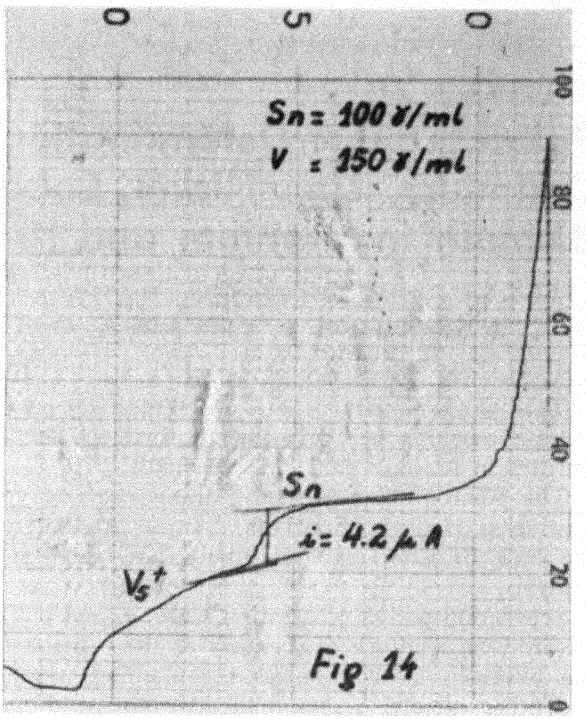

Figure 14

Tungsten does not interfere with the polarography of tin (Fig. 12).

Tantalum does not interfere with the determination of this element (Fig. 13).

Vanadium does not interfere with the polarography of tin (Fig. 14), except when present in great excess.

Although various elements interfere with the polarographic determination of tin, their number is considerably reduced in the prior stages of separation (Table II).

Consequently, the only element of those considered that could be troublesome in the proposed method is (Fe(III); this interference is eliminated by conversion to Fe(II) using hydroxylamine.

SUMMARY

A polarographic method is proposed for estimating tin in uranium and its compounds.

This element is separated from almost all the possible interferences by extracting its cupferrate with chloroform in an acid medium and then precipitating it as the hydroxide in the presence of aluminum.

A study is made of the possible interferences, leading to the conclusion that in the final stage only iron may be troublesome; this drawback is remedied by reducing the latter with hydroxylamine.

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Polarographic Determination of Copper, Cadmium, Zinc, Nickel, Cobalt, Lead and Bismuth in Uranium and its Compounds

By C. J. Sambucetti, E. Witt and A. Gori,* Argentina

This work is part of the program for studying minute amounts of the elements forming the impurities in uranium and its compounds.

The polarographic method requires previous concentration of these impurities, their separation from the bulk of uranium, and finally, the quantitative analysis.

Separation and concentration were carried out by electrolysis. The use of mercury as the cathode for the electrolysis of a solution containing uranium and other metals, causes, under certain conditions, the contaminants to deposit in the mercury and the uranium to remain in solution. The next step is the separation by distillation of the metals amalgamated with the mercury, after which, the metallic residue is dissolved and analyzed by polarography.

This paper is based on work by Rodden[1] who suggests separation by electrolysis with a mercury cathode and recovery of the impurities by distillation.

No other details of the analytical process suggest that either the colorimetric or the polarographic method may be used.

Therefore, we became interested in evolving a method that would make polarographic analysis possible using the joint separation of the seven elements by electrolysis.

APPARATUS

A Melaven[2, 3] standard electrolytic cell with some modifications and a Tinsley automatic recording polarograph were used.

Figure 1 shows the details of the electrolytic cell.

ELECTROLYSIS AND DISTILLATION

The sample is converted into uranium oxide (UO_3). A suitable amount of it then is dissolved in perchloric acid to make a 1*N* solution. This is transferred to the electrolytic bath containing 20 ml mercury; electrolysis is carried out for two hours using a current of 1–2 amperes and the temperature is maintained at about 25°C by cooling the cell with water.

Samples containing from 5 to 10 gm uranium in 90 ml solution were electrolized.

For the electrodes, the anode was a flat platinum wire coil just submerged in the electrolyte; the cathode is the mercury with a platinum lead attached to the wall of the cell.[4]

The mercury from the cell was collected in a quartz or Pyrex crucible at the end of electrolysis, and distilled in nitrogen.

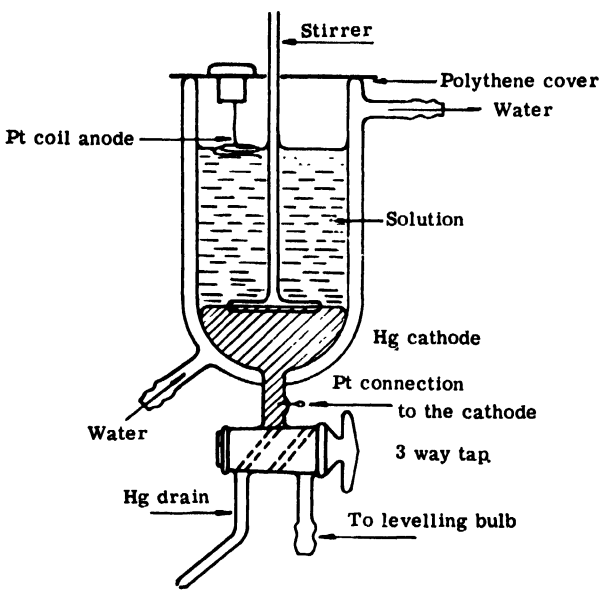

Figure 1. Electrolytic cell

The residue from the distillation was dissolved in hot nitric acid and made up to 25 ml. Aliquot quantities of this solution were used for the polarographic analysis of the elements under study. The seven values could be obtained in three polarograms taking into account the characteristics of each element.

DETERMINATION OF COPPER, CADMIUM, AND ZINC

A medium containing 1*N* ammonium chloride, 1*N* ammonia, and 0.005% gelatine[6] is the most convenient for the determination of these three elements. The cupric ion produces two waves in this medium; the first one corresponds to the cupric-cuprous reaction and produces a — 0.24 volt potential; the second wave corresponds to the $Cu^{I} \rightarrow Cu^{0}$ transformation and produces — 0.5 volts. The cadmium ions are

Original language: Spanish.

* Comisión Nacional de la Energía Atómica.

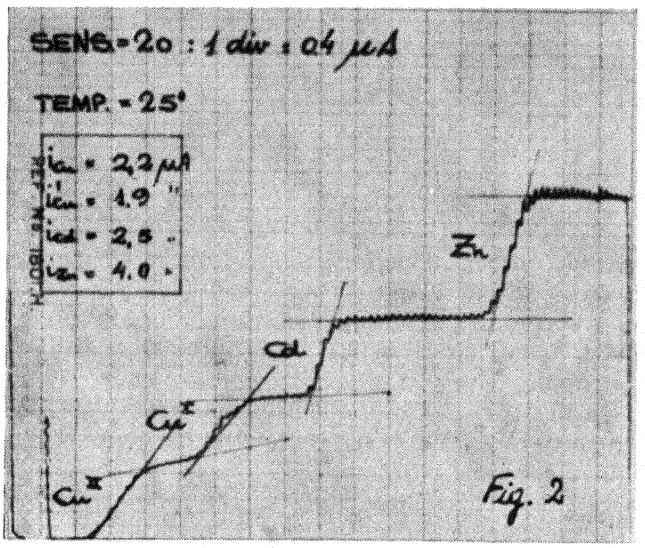

Figure 2

deposited at — 0.81 volts, while zinc generates a — 1.33 volt wave.

The polarogram (Fig. 2) displays a well defined separation of the three waves. The second wave is selected for the evaluation of copper since it is less affected by the residual current.

Copper, cadmium, and zinc standard solutions are prepared by weighing the pure metals, and contain 0.05 mg/ml; the necessary fractions for the construction of the calibration curve are used; the solutions are evaporated almost to dryness; 10 ml hydrochloric acid (1:1) is added to dissolve the residue which is then neutralized with ammonia, later adding 25 ml of 2*N* ammonium chloride solution and 2 ml of a recently prepared 0.1% gelatine solution, making the volume up to 50 ml.

The polarograms are constructed with these solutions. The following lower detection limits were obtained from the calibration curve (Fig. 3): copper, 2 γ/ml; cadmium, 2 γ/ml; zinc, 1 γ/ml.

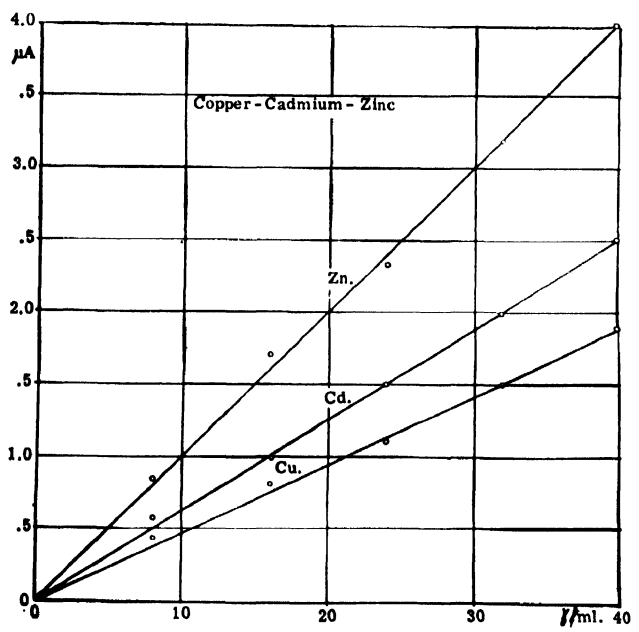

Figure 3. Copper-cadmium-zinc

Recovery tests followed the procedure described above; the results are given in Table I.

DETERMINATION OF LEAD AND BISMUTH

It must be noted that the evaluation of lead and bismuth is done jointly, and that the estimation of the latter by this method is described merely as probable in the references.[1]

The best medium for the joint polarographic determination of these elements is sodium tartrate at an adjusted pH and with an admixture of 0.005% gelatine; under these conditions waves for cadmium and copper are obtained so that the method may be used for the joint determination of the four ions.[7]

Table I

Element	*Added γ/ml*	*Recovered γ/ml*
Copper	20	19
	20	19
	20	21
	20	19
	20	21
Cadmium	20	19
	20	19
	20	18
	20	18
Zinc	20	20
	20	21
	20	21
	20	21

The order of appearance of the waves is as follows: copper: — 0.3 volts; bismuth: — 0.45 volts; lead: — 0.70 volts; and cadmium: — 0.9 volts, approximately, as may be seen from the polarogram (Fig. 4).

It must be noted that the pH of the medium has a considerable effect, not only the shape and the regularity of the wave, but also the redox potential of the elements.

The solution containing the ions to be evaluated is dried, 25 ml 1*N* tartaric acid is added and it is heated until it dissolves; the pH being adjusted at 3.5–4.5 with 2*N* sodium hydroxide; bromo cresol green is used as indicator. The solution is diluted to 50 ml.

Calibration curves (Fig. 5) for typical solution of each element are constructed.

From these calibration curves it may be seen that

Table II

Element	*Added γ/ml*	*Recovered γ/ml*
Lead	20	21
	20	21
	20	19
	20	21
Bismuth	20	21
	20	19
	20	21

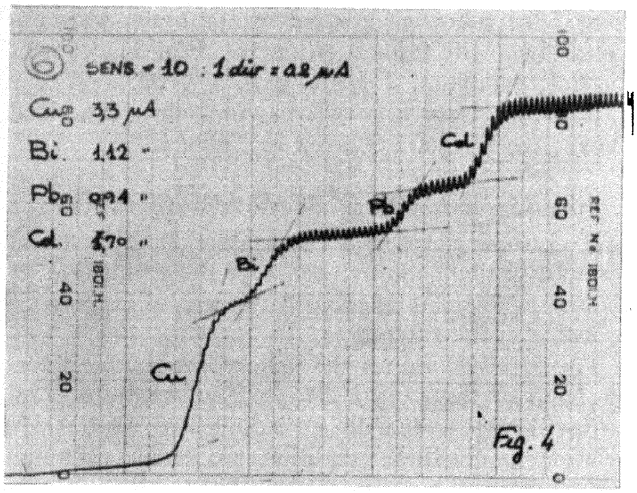

Figure 4

the lower detection limits of these elements are: lead, 2 γ/ml; bismuth, 2 γ/ml.

Recovery experiments were made; the results appear in Table II.

DETERMINATION OF COBALT AND NICKEL

Potassium chloride and pyridine were used as carriers for the evaluation of these elements.[8]

Pyridine has the property of forming complexes which are similar to the ammonia complexes with certain cations. The formation of these complexes makes possible, under certain conditions, polarographic separation of nickel and cobalt, since each element has a characteristic and distinct decomposition potential.

Table III

Nickel			*Cobalt*		
Added γ/ml	*Intensity* μa	*Found* γ/ml	*Added* γ/ml	*Intensity* μa	*Found* γ/ml
16	0.35	14	16	0.43	16
25	1.8	26	25	2.0	26
40	2.9	41	40	3.0	39

In this particular case, it can be asserted that this property offers the best process for the joint determination of the two ions.

If a 0.5*M* pyridine solution in 1*M* potassium chloride containing 0.05% gelatine is used, nickel produces a wave at a potential of about — 0.17 volts and the cobalt at about — 1.07 volts. But, under these conditions, the cobalt wave shows a typical and well defined peak which, according to some authors, is eliminated by the gelatine admixture;[6] however, even if the gelatine concentration is increased ten-fold, the peak persists despite the fact that the above mentioned conditions are maintained with all the inconveniences resulting from the high gelatine concentration.

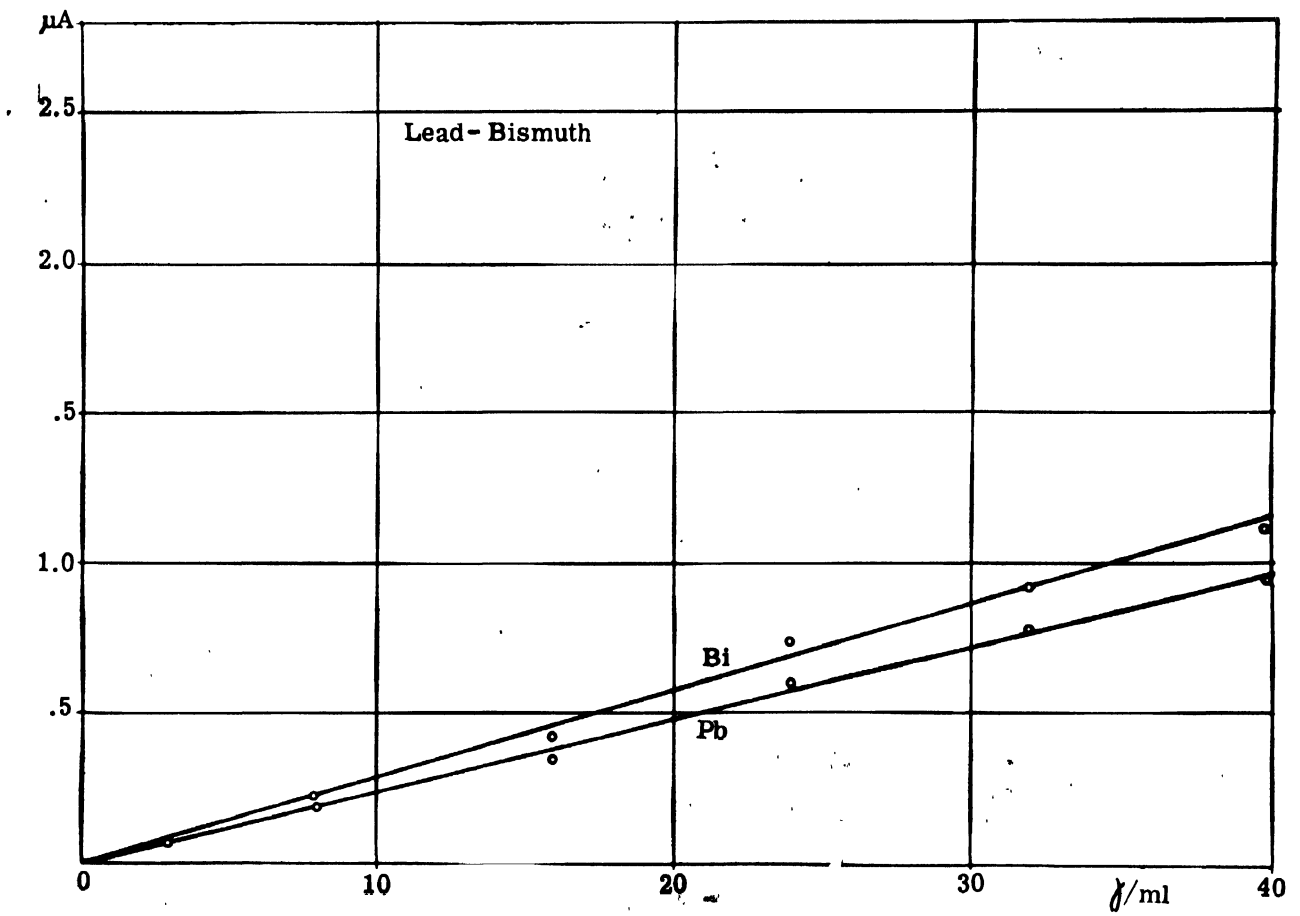

Figure 5. Lead-bismuth

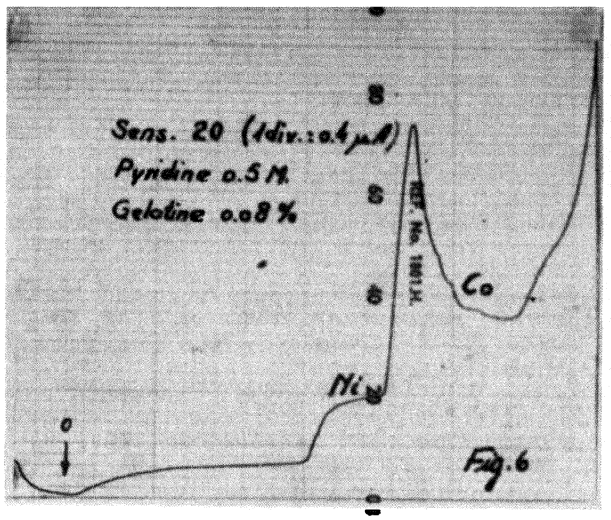

Figure 6

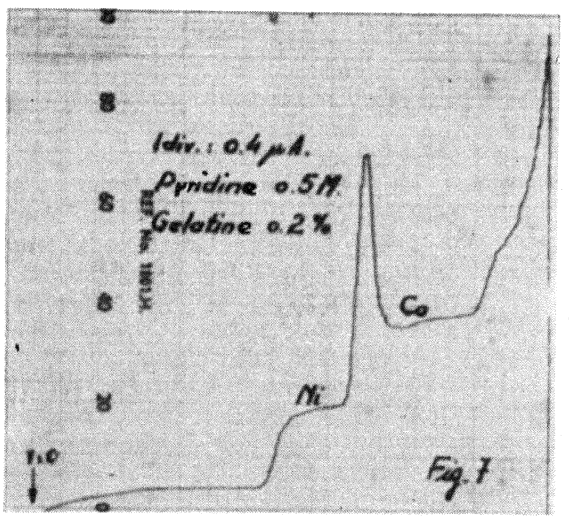

Figure 7

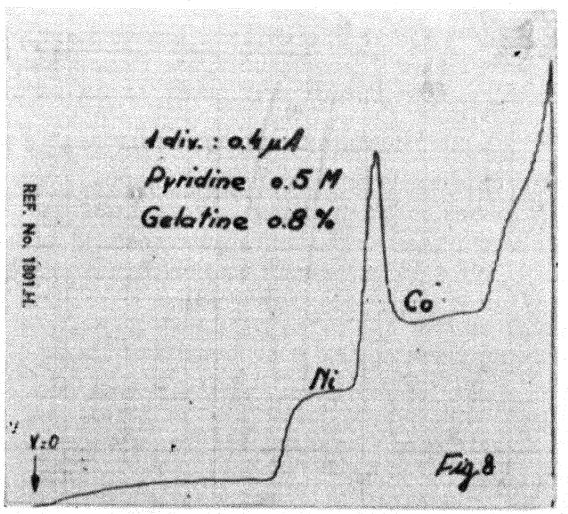

Figure 8

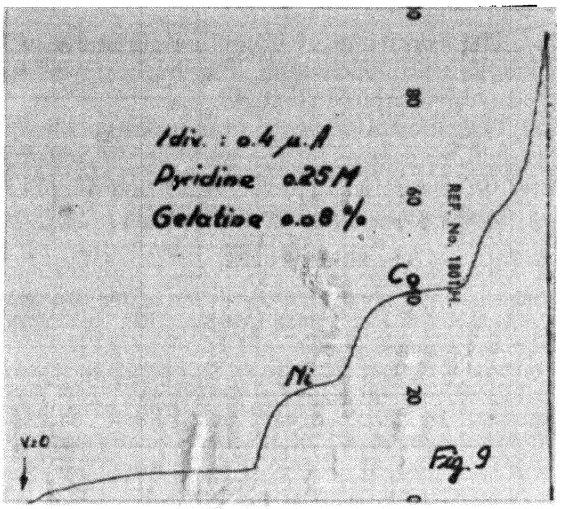

Figure 9

It was found that, by maintaining a constant potassium chloride concentration, but decreasing the pyridine to 0.2*M*, the peak disappears when gelatine at a 0.08% concentration is used. A wave, very regular and undistorted, is obtained in this fashion (Figs. 6, 7, 8, and 9).

To the aliquot parts in which these ions are to be evaluated, are added: 6 ml potassium chloride 4*N*, 0.5 ml pure pyridine (d: 0.98) and 2 ml 1% gelatine, and making up to 25 ml volume.

The calibration curves (Fig. 10) were constructed with typical solutions.

According to these curves, the detection limits for these elements are: cobalt, 1 γ/ml; nickel, 1 γ/ml.

Table III includes the results obtained in a series of recovery tests.

CONCLUSIONS

The joint deposition of copper, cadmium, zinc, cobalt, nickel, lead, and bismuth by electrolysis with a mercury cathode is used in this work for the ultimate polarography of these elements.

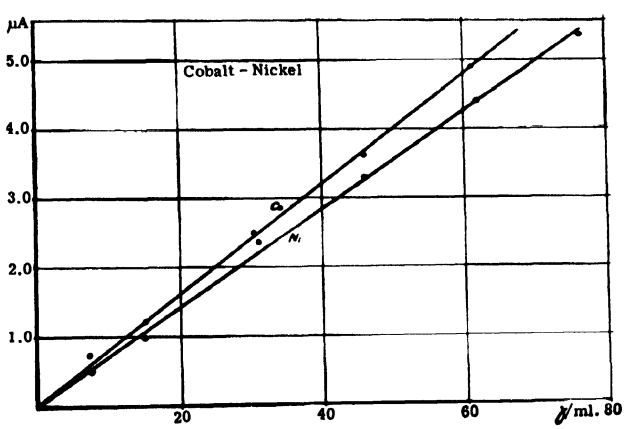

Figure 10. Cobalt-nickel

It was demonstrated that:

(*a*) The evaluation of bismuth in uranium or its compounds can be achieved. Previously it was considered only as a possibility.

(*b*) The elimination of the peak in the cobalt wave is possible by decreasing the pyridine concentration instead of increasing the gelatine concentration; the latter procedure has not been effective.

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Contributions to Methods of Measuring the Concentrations of Uranium and Thorium in Minerals (Nuclear Emulsions)

By A. Soltan,* Poland

Measurements of the concentration of uranium and thorium in various rocks by the nuclear emulsion method are systematically undertaken in Poland. This work began under the late M. S. Piénkowski and is being continued by some of his collaborators.

Studies of granite have shown that its radioactivity is due chiefly to inclusions of biotite and zircon. About 95% of the tracks of alpha particles are concentrated in 2–3% of the aggregate surface of the piece of granite under investigation. Thorium stars have been observed in the neighborhood of the biotites and zircons, which is not the case in the neighborhood of iron oxide crystals.

The zircon crystals, which produce a comparatively low number of alpha tracks, have not produced any changes in the biotite that surrounds them: the zircon crystals that exhibit a higher concentration of radioactive substances are surrounded by a double sheath. The first one is transparent, while the second consists of a darker layer of biotite crystal.

It should be added that investigation by the nuclear emulsion method of transparent sheets of granite containing sheathed zircons might be used in developing a method to establish the approximate age of rocks. Formation of a sheath depends upon the number of alpha particles emitted by the radioactive substances within the zircon and upon the time during which they have acted upon the crystal lattice surrounding the zircon.

Studying the radioactive properties of phosphorites is of special interest, both for their origin and evolution and for analysis of the migration and localization of radioactive substances.

METHOD OF MEASUREMENT

Since it could be predicted that the radioactivity of the phosphorites would be low, we employed the Geiger-Müller counter method, suitably modified, or the method of nuclear emulsions, or a combination of both.

In the first method, a pellet (14 mm in diameter and 3 mm thick) molded from the finely pulverized phosphorite sample served as the source of radiation. It was placed at a distance of 0.4 mm from the mica window of the counter. The window, 2.4 mg/cm^2 thick, allowed the alpha rays to pass. The pulses were recorded appropriately.

The pulses due to the alpha rays could be distinguished from those produced by beta and gamma rays by insertion of 50 μ of Al.

The impulses were suitably recorded by a scaler.

These measurements were compared to the radiation of a standard substance, whose uranium concentration had been determined by counting the alpha particles emitted through the solid angle 4π per unit of time by a known quantity of the substance which was reduced to a fine powder and placed between two layers of the nuclear emulsion.

These data enabled us to compute the concentration of uranium in the specimens investigated. Once we knew this value, we could calculate the quantities of all the other elements in the two radioactive families. The values of the uranium concentration $C(U)$ thus obtained are correct provided the ratio $C(Th)/C(U)$ is essentially the same for all the specimens and their chemical composition does not depart appreciably from the mean, which is usually the case. It should be noted, however, that it is often very hard to tell how representative the specimen under investigation is of the mean properties of its environment, in view of the heterogeneity of the latter, which varies but is always appreciable. Study of the distribution of radioactive substances in ores has shown the importance of this factor. Nevertheless, the series of measurements made on the same sample did not vary by more than 5 to 8% in the specimens under investigation here. There is no doubt that specimens taken from different points of the same stratum would exhibit larger differences. (It should be noted, however, that specimens 5, 6, and 7 in Table I were taken from analogous strata of adjacent geological levels, though the locations were more than 200 km apart. Nevertheless, their uranium concentrations did not differ by more than 4%.)

RESULTS OF MEASUREMENTS

Study of the activity of specimens of various origins has shown that all these phosphorites contain radioactive substances, but that their activity differs considerably.

The table given below lists the typical phosphorites we have investigated, their location in the geological formations, and an approximate estimate of their

Original language: French.

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age. The last column gives the value of the uranium concentration $C(U)$ in arbitrary units.

These figures indicate that the phosphorites we have investigated possess appreciable radioactivity, varying within comparatively wide limits (from 3.7 to 138.7). We also note, however, a marked tendency for the activity to vary with age of the ore.

Table I

Specimen	*Geological stage*	*Age, in 10^6 years*	*$C(U)$, arbitrary units*
1	Middle Cambrian	400	3.7
2	Middle Cambrian	370	9.4
3	Upper Ordovician	350	5.3
4	Lower Cenomanian	100	63.0
5	Lower Cenomanian	100	46.0
6	Middle Cenomanian	95	47.6
7	Middle Cenomanian	95	47.8
8	Maestrichtian	75	138.7
9	Upper Cretaceous	60	132.5

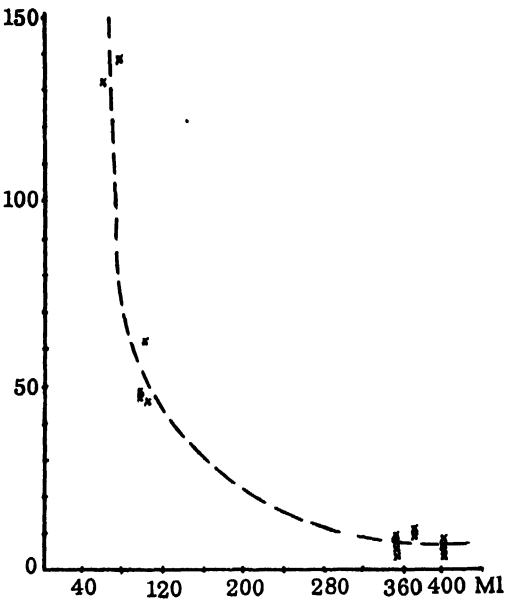

Figure 1

The very old phosphorites are only slightly radioactive. However, their activity increases progressively for the younger formations. The curve shown in Fig. 1 gives the variation of the uranium concentration $C(U)$ as a function of the age attributed to the geological formation. The existence of such a relationship between the content of radioactive substances and the age of phosphorite is interesting. It may be due either to the conditions prevailing at the time the deposit was formed or else to the way in which it has developed. Several hypotheses may be advanced to explain the course of this curve. But it seems that it is too early for substantiated interpretations. Research now under way promises to yield new data.

A Method for the Measuring of Uranium and Thorium Using Nuclear Emulsions

By M. Petrascou and C. Besliu,* Rumania

We use the emanations of uranium or thorium for the estimation of these elements by means of nuclear emulsions.

The procedure is more sensitive than the ionization chamber and electrometer procedures and affords means of getting a direct evaluation of the ratio of

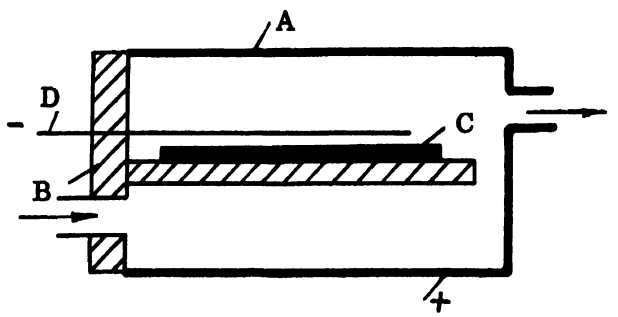

Figure 1. (A) metallic cylinder; (B) insulating material; (C) photographic emulsion; (D) metal wire

these two elements which may be present simultaneously in the ores to be analyzed.

The nuclear emulsion is placed in an area where an intense field exists, close to a wire which is maintained at a suitable negative potential.

The emanation in question is carried, in a closed circuit, by a current of dry air, into the area of the photographic emulsion.

Part of the products of the active deposit, carried by the field, will adhere to the emulsion.

The number of tracks per square cm, in a suitably chosen area, will give the concentration of the element under consideration.

The device is calibrated by means of a known source.

The photographic plate is placed parallel to the wire (Ag or Pt), and in its immediate vicinity (Fig. 1).

The track distribution, in narrow sections normal to the wire, as a function of the distance α from its end (Fig. 2), offers a very convenient plateau over almost the whole length of the plate.

The number of tracks per square cm increases with the voltage maintained in the wire, and reaches saturation for a potential which is a function of the assembly spacing.

In our devices, the optimum voltage varied between 200 and 500 volts.

In the plateau range, the number of tracks per square cm varies in proportion to the amount of emanation present in the product to be analyzed, when work is carried out under identical conditions.

For instance, in an experimental case, there will be recorded in the range of the plateau, 2200 tracks per cm^2 at a voltage of 440 volts and a radium content of 1.8×10^{-12} gm.

We were able to measure up to 5×10^{-14} curies with an error of $\pm 6\%$.

The method is less speedy than those making use of the ionization chamber and electrometer: it has the advantage of being simple and of allowing for

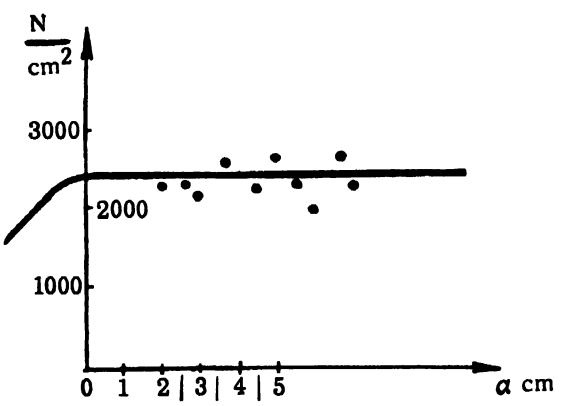

Figure 2

the simultaneous identification of the substances involved. This may be useful in certain cases.

The device can easily be decontaminated between two measurements.

It may be useful for periodic checking of activity in uranium and thorium mines, as well as for the analysis of the air in the vicinity of chemical plants engaged in the separation of these elements.

Original language: French.

* "Structure of Matter" Laboratory, University of Bucharest.

The Employment of Liquid Emulsion for the Estimation of Uranium from Radioactive Minerals

By F. A. G. A. Brandão,*† Elisa Frota-Pessôa,* Neusa Margem* and Waldyr Perez,*‡ Brazil

In the present paper[1] a method for the estimation of minerals in solution is described, in which the solution to be estimated is mixed with liquid nuclear emulsion. The slide obtained is compared with another one, containing a standard solution, prepared under analogous conditions.

Only minerals which do not contain members of the Th^{232} family are considered here.

From the analysis of the two slides referred to above we obtain the ratio of the number of uranium atoms contained in equal quantities of the radioactive mineral solution and the standard solution. Knowing the number of uranium atoms per unit volume for the standard solution, one can determine the corresponding number for the mineral solution and therefore the U^{238} content of the mineral.

Considerations about the diffusion of radioelements in nuclear emulsion are also made.

Due to the increase of interest in the estimation of uranium and other radioelements, especially from minerals with a low content in these elements, several methods of estimation have been recently developed utilizing nuclear emulsions.

In the existing methods for the estimation of minerals in solution, ready-made slides are being used. In the present work a method is developed by which the solution to be estimated is mixed with liquid emulsion; the slide thus obtained is compared with another slide prepared under analogous conditions but containing a standard solution.

We shall limit ourselves here to the case of minerals which contain elements solely of the uranium family. The estimation of minerals which contain both the thorium and uranium families, or the thorium family alone, will be the subject of a later study.

METHOD OF TITRATION

The mixture of the liquid emulsion and the standard solution of uranium salt is evenly spread out on a glass slide, and on another identical slide the mixture of liquid emulsion and mineral solution is spread. The two slides should be prepared jointly in order to make the comparison: equal masses of the emulsion and equal quantities of the solutions should be used. After having dried, the slides are left in a refrigerator for several days' exposure, and are then developed.

Before making the comparison between the two slides, histograms should be made of the number of alpha particles *that do not form part of stars*, versus the range in the emulsion, both for the standard solution and for the unknown solution. This histogram determines, by analysis, the percentage of radioactive elements present.

Figure 1 represents the histogram obtained with a solution of uranyl acetate (Baker) used as standard. It can be seen that there are two groups of alpha particles with practically the same number of tracks; the first group corresponds to U^{238} and the second group to U^{234} and U^{235}; this is the result expected for chemically pure uranium salts. Indeed U^{238} and U^{234}, being in secular equilibrium, do emit the same number of particles per second denoted by n. Also, since the isotopic composition of uranium is 99.28/0.0057/0.71 for $U^{238}/U^{234}/U^{235}$, and the decay period of U^{235} is one fifth that of U^{238}, there will be $0.035n$ particles per second emitted by U^{235} in the second group. The total number of alpha tracks then is 2.035 times the number of alpha particles due to U^{238}. The histogram of the standard solution should be made in order to verify its composition once and for all.

Figure 2 gives the histogram of a uranium mineral (uraninite from Brejaubas) which does not contain the thorium family. This is seen by the fact that no thorium stars were observed. One sees that there are three groups of alpha tracks: a first group corresponding to U^{238}; a second group three times larger than the first, corresponding to U^{234}, Th^{230} and Ra^{226}; and a third group due to Po^{210}. In the present case Ra^{226} gives mainly single alpha particle tracks in view of the large diffusion of the radon which is produced.[1] If the Rn did not diffuse, stars would be produced. Appendix I indicates the method used in treating those cases in which Ra^{226} does not give single tracks. It is found that, within statistical errors, the polonium group contains the same number of particles as the U^{238} group. This is frequently the case with compact rocks, when there is no appreciable loss of Rn. In these cases (and this

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paper is restricted to such), there is no need for making out the histogram of the mineral. The total number of single tracks is then 5.1 times the number of the U^{238} tracks. This includes the tracks corresponding to U^{235}, Pa^{231} and Th^{227} in secular equilibrium which contribute to the second and third group (and amount 3×0.035 for the number of U^{238} tracks).

For the estimation itself, one proceeds in the following manner:

First, a count of the number of alpha particle tracks per microscopic field on the slide is made for the standard solution. The counting is done for various fields and the arithmetic average N_S is obtained. $N_S/2.035$ is the mean number of alphas per field due to U^{238}.

For the slide containing the mineral solution, a count is also made of the number of alpha particle tracks present in a microscopic field but *not* belonging to a star. The average rate in this case is denoted by N_m. The ratio $N_m/5.1$ is the mean number per field of alphas due to U^{238}.

Since the time of exposure is the same for the two slides, one gets the approximate value r, where

$$r = \frac{2.035\, N_m}{5.1\, N_S} \qquad (1)$$

for the ratio of the number of uranium atoms contained in equal quantities of the radioactive mineral solution and the standard solution.

Knowing the number of uranium atoms per unit volume for the standard solution, one can then determine the number for the mineral solution, thus obtaining the U^{238} content of the mineral.

Once this content is known, the corresponding quantity of radium can be calculated, using the equation for the secular equilibrium:

$$\lambda_a N_a = \lambda_b N_b \qquad (2)$$

λ_a and λ_b being the constant of disintegration of uranium and radium respectively; N_a the number of uranium atoms; and N_b the number of radium atoms in the given mineral mass.

If there is sizable diffusion of Rn in the rock, the average number of tracks per field, due to U^{238}, is obtained for the slide with mineral solution in the following way: one multiplies the average number of single tracks per field, by T_1/T, where T_1 is the number of particles belonging to the U^{238} group in the histogram of the mineral, and T is the total number of particles in the histogram.

RESULTS OF OBSERVATION

In order to verify the method, we have made the following measurements:

Comparison between Three Solutions of Uranyl Acetate (Baker) of 1/500, 1/1000 and 1/2000 Concentrations

For the counting, 100× objective and 6× eyepieces were used and approximately 1000 tracks were counted. The result of the measurements is shown in the graph in Fig. 3. Taking the 1/500 solution as standard, the concentrations 0.00098 ± 0.00003 and 0.00048 ± 0.000015 were obtained for the 0.001 and 0.0005 solutions respectively. (The errors indicated are probable errors.)

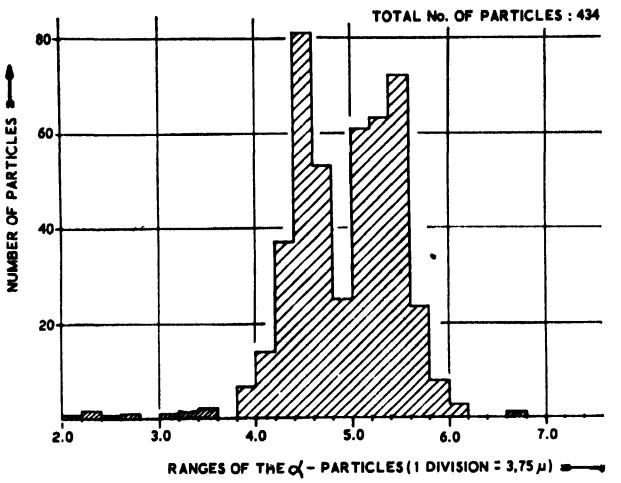

Figure 1. Histogram showing the distribution of ranges of α-particles from uranyl acetate. Total number of particles: 434

Estimation of a Uranyl Nitrate Solution (Baker), Taking as Reference a Solution of Uranyl Acetate

The concentration of the acetate solution used was 1/4000 and that of nitrate, 1/1000. The result obtained for the concentration of nitrate was 0.001 ± 0.00003. 45× objective, and 6× eyepieces were used, and about 1000 tracks were counted. It was assumed that in the nitrate there were only U^{238}, U^{234} and U^{235} isotopes as for the acetate, since both salts came from the same laboratory.

Determination of Radium Content in the Uraninite from Brejaubas (Minas Gerais)

The solution used as standard was 1/4000 uranyl acetate (Baker). The histogram of Fig. 3 was obtained for the mineral solution. It showed about 200 alpha particles which did not belong to the elements U^{238}, U^{234}, Th^{230} and Ra^{226} (the majority of them were due to Po).

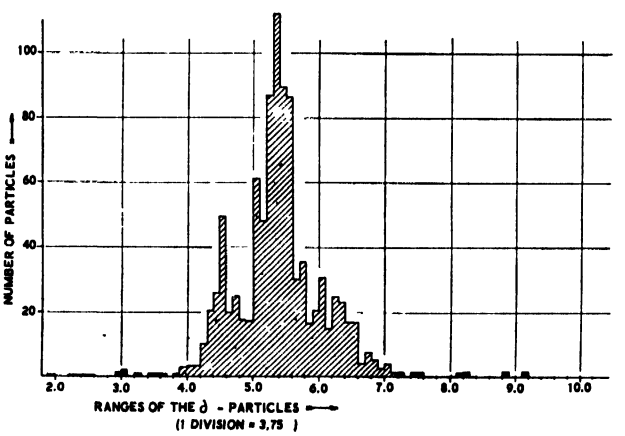

Figure 2. Histogram showing the distribution of α-particles from the radioactive mineral. Total number of particles: 956

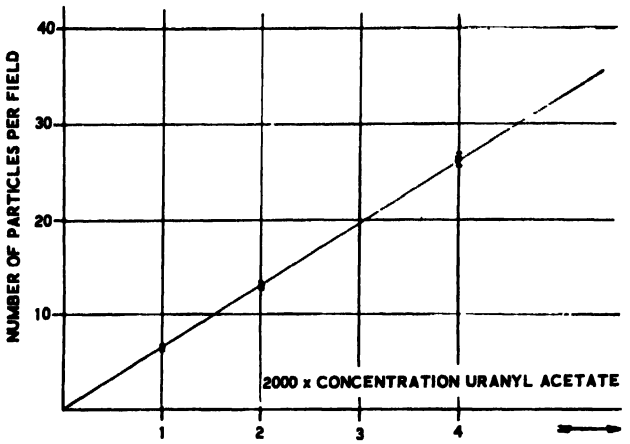

Figure 3. Graph of the mean number of particles per field of view of the microscope as a function of the concentration for a solution of uranyl acetate

In measurements made in two slides employing the same $1/2000$ mineral solution, the results obtained were 275 and 263 mg of radium per ton (1000 track counts made per slide).

These results are in accordance with those of Costa Ribeiro,[3] who obtained for this mineral a content of 253 mg of radium per ton, with individual values ranging between 232 and 273 mg.

In all the measurements, the time spent between the preparation of the slides and their development was approximately three days.

PREPARATION OF THE SOLUTIONS

Considering that the neutrality of the solutions of the uranium salts used is important to guarantee the sensitivity of the nuclear emulsion,[4] all the radioactive solutions employed were neutralized after being previously treated with citric acid. This acid forms a complex with the uranium[5, 6] and avoids its precipitation when the solution is neutralized by ammonium hydroxide.[7]

PREPARING THE SLIDES

From a sheet of glass of uniform thickness (preferably one prepared by Ilford especially for nuclear slides), the slides are cut into the dimensions desired. A surface of approximately 22.8 cm^2 was used in the present work. The slides are then weighed on an accurate scale, the reason for the weighing being obvious from what follows:

Given masses of the solutions to be compared are mixed with known masses of the emulsion. The weighing of the emulsion and of the solution is recommended as being more precise than measuring the volume; for instance, the measurement of 0.5 cm^3 of solution with a precision pipette of 0.1 cm^3 is susceptible to an error of 2.5%. Nearly two grams of emulsion and about 0.5 cm^3 of solution were used per slide.

Place the mixture in a bath at 51°C for 20 minutes in order to melt the emulsion; stir it with a glass rod. Spread the liquid over the slides which are placed on a level plane, and then leave them to dry. To facilitate drying, the plate containing the slides may be warmed a little by putting a lamp beneath it and by using a ventilator in order to circulate air over the emulsion.

To compare the thickness of emulsion in the several slides, weigh the plates again after drying. The relation between the mass of emulsion and the mass of the glass gives a number proportional to the thickness of the emulsion. This number allows one to reduce the results of the counting in the several plates to the same thickness.

DEVELOPING AND FIXING

1. Developer was:[8] distilled water 1000 cm^3; boric acid, 35 gm; sodium sulphite (anhydrous), 18 gm; potassium bromide (10% solution), 8 cm^3; amidol, 4.5 gm. Developing time was 20 minutes. Developing temperature was 28°C.

2. Stop bath was 0.2% acetic acid solution. Time was one hour; temperature was 28°C initially, gradually lowered to 4°C.

3. Fixing bath was 40% sodium hyposulphite solution at a temperature of 10 to 15°C. After fixing, the slides are washed in water at 10°C, which is renewed each half hour.

COUNTING

A field is selected, with a diameter which is large in relation to the range of the particles. Count the tracks within the field, and to this number add half the number of those tracks not entirely contained within. This sum is the number of tracks per microscopic field, referred to in the titration method.

CONCLUSIONS

The method of estimation developed in the present work gave a 3% precision in the conditions of our measurements.

The following advantages of the present method over other methods of estimation with emulsion are apparent:

The fact that there is absorption of alpha particles only by the emulsion itself presents an advantage over those methods in which the solution is not placed directly, in the emulsion.[9]

The advantage over the drop method is that in this case it is not necessary to count all tracks in regions where the solution is present on the plates.

The method of soaking ready-made plates in solution presents difficulties concerning the equilibrium of the concentrations between solution and nuclear emulsion[11] and the velocity of diffusion of different elements in the emulsion[12], difficulties which do not appear in the present method.

ACKNOWLEDGEMENTS

We are grateful to Dr. Alexander Girotto for facilities in his laboratory at the Departamento de Produção Mineral, and to Professor J. Costa Ribeiro, who gave us the samples of the Brejaubas mineral. We are also indebted to Professor G. Occhialini for interesting discussions.

APPENDIX

Correction for diffusion and long time exposures

Equation 1 for the ratio r of the number of uranium atoms in the mineral solution and in equal volume of the standard solution does not take into account the following facts: non-diffused radon; diffusion of radon decay products; and influence of exposure time.

Non-diffused radon

If the Rn^{222}, resulting from the disintegration of Ra^{226}, does not diffuse, a 4-branch star will be produced instead of a single track as assumed in Equation 1. This is not important in our case as can be seen from the following fact: If all Rn^{222} were retained, then 20% of the disintegrated Ra^{226} in the emulsion would give rise to 4-branch stars for a 3 days' exposure.[13] In our case, for three days' exposure, only 2% of such stars were produced.

Diffusion of radon decay products

When Rn^{222} disintegrates in the emulsion, not only 3-branch stars can be produced but also 2-branch stars with a nearby single track.[13] This is due to the diffusion of Bi^{214} and (or) Pb^{214}. These single tracks were not considered in the deduction of Equation 1. In the present case the error due to these tracks is small, because most of the diffused Rn^{222} leaves the emulsion.

Influence of exposure time

For long exposure times, not only the effect of the non-diffused Rn^{222} increases, but also a new source of error appears. This is due to the fact that Ra^{223}, resulting from Th^{227}, has an 11.4 day half-life. So for long exposures besides the single tracks from Th^{227} also 5-branch stars will be produced, and a small error will be introduced, if Equation 1 is used.

The correct formula, taking into account the facts above referred to, is:

$$r = \frac{2.035\, N_m'}{5.14\, N_s} \qquad (3)$$

Here N_m' is the average number per field of: *single tracks* plus *4-branch stars* plus *twice the 5-branch stars* minus *2-branch stars*.

This formula is obtained by a detailed examination of all the configurations of tracks that can occur in the emulsion taking into account all the existing radioelements and their known diffusion properties. We do not take into account the possible diffusion of Rn^{219} in view of the short lifetime (4 sec) of this element.

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Chromatographic Determination of Uranium in Various Materials

By D. I. Ryabchikov and M. M. Seniavin, USSR

The methods of preliminary isolation of pure uranium are very important (equally to selective methods of direct determination) for the quantitative analysis of materials, containing uranium.

The chromatographic method elaborated by Tsvet[1] in 1903 has found, along with extraction, extensive application in recent years among the methods mentioned above.

The chromatographic method of separating mixtures assumes a relative movement between sorbent and mixture to be analysed.

Arising as a result of the original generalization by Tsvet of achievements in the sphere of sorption phenomena[2] this method evolved naturally as a particular case of a simple dynamic method of separating a known solution. Therefore, unlike Samuelson's concept,[3] we shall not make a sharply marked distinction between simple dynamic methods of ion exchange and ion exchange chromatography.

The extensive application of the chromatographic method, first to the investigation of the composition of plant pigments and later in numerous branches of analytical chemistry, began essentially in the thirties. Thousands of investigations dealing with the application of this method in analytical practice are known nowadays. The utilization of this method is aimed, as is known, at isolating the necessary component in a pure state; further quantitative determination of the isolated element is performed by means of common chemical or physicochemical methods[4] even non-specific for the element. The chromatographic method may be utilized both for analytical and preparative purposes and it has been already applied in a number of branches of fine chemical technology and hydrometallurgy. In a chromatographic experiment carried out under proper conditions the precision and sensitivity of the analysis depends, on the whole, on specific features of the method applied for determining the elements (including uranium).

Accumulation of profound knowledge in fields adjacent to chromatography has greatly promoted a rapid development of the chromatographic method. Some researches on the dynamics of sorption should be mentioned in this connection. The chief principles of the dynamics of sorption of gases and vapours with the utilization of active carbon were formulated by Shilov as far back as 1916. The main results of these researches were published in 1929.[5] The investigations showed that in dynamic conditions a parallel shifting of the sorption front is established in the sorbent bed. Later Dubinin[6] discovered that the distortion of the front is due to kinetic factors. The complete quantitative theory of the dynamics of adsorption was given by Zhukhovitsky, Tikhonov, Zabezhinsky[7,8] and others. It followed from this theory that a parallel shifting takes place when we have a convex isotherm. These authors revealed a relative role of internal and external diffusion and showed that the greater the coefficient of sorption the more manifest is the role of external diffusion. This conclusion was later proved by many experiments on sorption of gases and solutes, the results of which coincided with theses of this theory.

The proper choice of sorbents is of great importance for the chromatographic separation. In view of this, a number of investigations have been carried out to study sorbents. Kiselev[9, 10, 11] elaborated an adsorption-calorimetric method of studying the structure of adsorbents. The results obtained proved that the skeleton structure of silica gel is shaped in the main trough the adhesion of separate colloid micelles of silicic acid. The absolute values (per unit of surface) of adsorption and of the adsorption heat in respect to quartz and silica gels of various porosity were established.

The influence of changes in the chemical nature of surface and the influence of the narrowing of pores were separately studied; the reasons that accelerate the adsorption in narrow pores for a number of substances were also found out.

An immense quantity of sorbents is now used in chromatography. According to their nature and, consequently, to the mechanism of interaction between the sorbents and the components of the mixture to be analysed, the scientists distinguish adsorption, ion-exchange and distribution chromatography. The ion exchange and distribution chromatography are of prime importance for the separation of ion mixtures. This report is devoted to the application of these kinds of chromatography for isolating uranium.

Original language: Russian.

ION EXCHANGE CHROMATOGRAPHY

A high separating capacity of the chromatographic method is demonstrated, for example, by the experiments on the chromatographic separation of mixtures of rare earths and isotopes. It is essential that this method makes it possible to separate mixtures with any ratio of components. Laskorin and Ulyanov have succeeded in working out an effective ion-exchange method of separating radium from barium. The high effectiveness of the chromatographic separation is first of all due to the multiplicity of single passes between the components of mixture and the sorbent, which is so essential to this method. Of course, it is clear that the value of the enrichment coefficient obtained in a single pass, is also significant. In the separation of ion mixtures the value of the coefficient is determined by the nature and properties of sorbent as well as by the chemical and physico-chemical properties of elements which are of great importance for choosing the optimum conditions for carrying out a chromatographic experiment. Since there is a considerable difference in chemical properties between uranium and the impurity elements, the mixtures can be separated, in most cases, through a single passage of the given solution with sorbent under dynamic conditions.

The laws of statics of ion exchange on which the ion exchange chromatography is based, were first formulated by Gedroyts[12] and constituted the core of his teaching on the absorbing capacity of the soil.

The consideration of ion exchange as a heterogeneous reaction which is governed by the law of mass action enable Rakovsky[13] and other researchers to establish the interdependence between the amount of sorption and the concentration of substances in solutions. The equation suggested, for example by Nikolsky,[14] was confirmed by a large amount of experimental material. The theoretical laws, in the

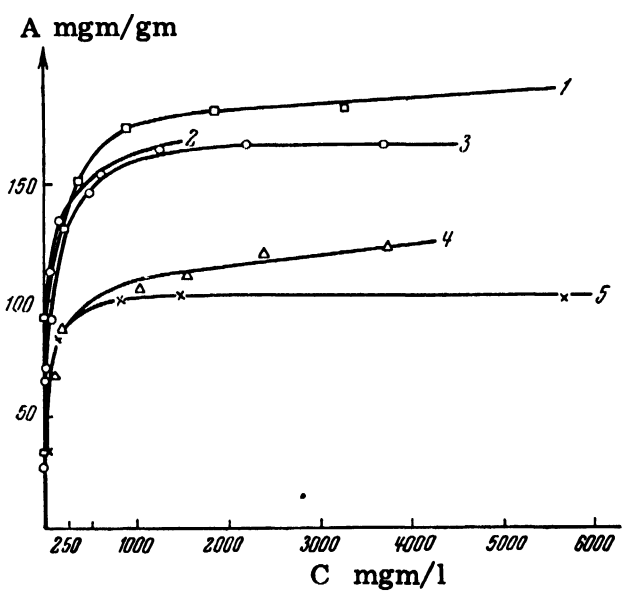

Figure 1. Isotherms of uranium by various cationites: (1) Wofatit KS; (2) SBS; (3) MSF; (4) Wofatit R; (5) sulfonated coal

sphere of the dynamics of sorption, established for physical sorption may, as it was found, be successfully applied to ion exchange. It was shown that when we have a convex (in respect to ions of external solution) isotherm, a parallel shifting of the front of sorption takes place, as is seen from Shilov's formula. For ion exchange in dilute solutions (large coefficient of sorption), the kinetics are determined

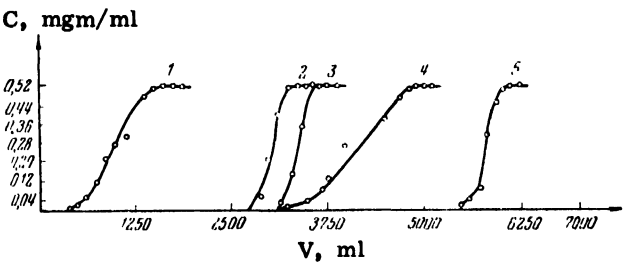

Figure 2. Elution curves of uranium for various cationites: (1) Wofatit C; (2) KU-1; (3) SBS; (4) RF; (5) KU-2

by external diffusion while in more concentrated solutions by internal diffusion. The determination of the diffusion coefficients of ions with several types of cationites was carried out in this connection.

In researches on the dynamics of ion exchange, scientists have also applied "plate" methods.

A number of investigations by Gapon[15] deal with these methods of calculation. Later, Tunitsky[16] showed that the "plate" method can to a certain extent account for the kinetics of sorption, too. Thus, comparing the precise solutions of the equations of sorption dynamics with the results of calculations by the "plate" method, it was found possible to establish the connection of the length, equivalent to a theoretical plate, with kinetic parameters (coefficients of internal and longitudinal diffusion, etc.).

Most of the researches on ion exchange chromatography are now carried out with synthetic ion exchange resins. Some data on their synthesis and properties are published in a number of papers.[17-21] It was found that for analytical purposes it is more expedient in many cases to use the cationate KU-2 (a sulfonated copolymer of styrene and divinylbenzene); this cationite has comparatively better kinetic characteristics. That is why the majority of experiments on the chromatographic isolation of uranium with the aid of cationites were carried out with the cationite KU-2; cases of the employment of other cationites are given below. Some experimental data on the absorption of uranium under static and dynamic conditions are shown in Figs. 1 and 2.

The separation of mixtures by the method of ion exchange chromatography is based upon the dependence of the sorption ability of ions, on the sign and value of the charge, as well as on the degree of hydration of ions. It is evident that the latter factor-difference in the degree of hydration is essential only for the separation of mixtures containing elements similar in their chemical characteristics (for example, mixtures of alkali metals) and less im-

portant for the elaboration of a method of the chromatographic separation of uranium from associated impurities. The separation of thorium from uranium, iron, aluminium, calcium, magnesium and copper,[22] and of uranium from iron and copper[23] is based on the dependence of the sorption properties of the ions and upon the value of their charge. The absorption of uranyl and thorium ions, under static and dynamic conditions, by a number of sulfocationites in the hydrogen, potassium and magnesium forms was examined in detail in a number of researches (Laskorin, Pesotskaya). The experimental data of the dependence of absorption value of ions of the above-mentioned elements upon the pH of the medium enabled the authors to determine the conditions for the ion exchange separation of mixtures of uranium and thorium containing equal or comparatively smaller amounts of thorium. Nikolsky and Trofimov have also discovered the selective absorption of thorium from 0.5–1.0*N*, solutions of hydrochloric or nitric acid. Such a separation is well accomplished in regard to both macro quantities of uranium and thorium, and mixtures containing tracer amounts of thorium. This method is a most simple and effective way of isolating the thorium isotope (UX_1) from uranium solutions. With the decrease of the concentration of hydrogen ions in solutions containing uranyl and thorium ions, the absorption of thorium ions by sulfocationite ceases earlier than the absorption of uranyl ions. When the pH of the solutions equal 3.8–4.5, we observe the selective absorption of uranyl ions and the separation of uranium from thorium becomes more complex and can be carried out only with a weak concentration of thorium in solutions. Such an experiment is performed only in a comparatively narrow interval of pH (3.8–4.5). When the index of pH is considerably higher or the concentration exceeds 5 gm/l, precipitation of thorium hydroxide occurs.

The methods of chromatographic separation of mixtures based on the difference in signs of the ion charge are most effective.

The nature of ion exchange resins (cationites or anionites) makes it easier to isolate in a pure state an element which can exist under proper conditions either in the form of a cation or an anion. Such an ability is possessed by the amphoteric elements and elements forming complex compounds in which the elements become part of the anion. It should be remembered that specific chromatographic conditions in this way allow the desorption of the elements only in the state of soluble compounds. Thus, knowledge of the chemical properties of the elements makes it possible to outline a number of methods for the ion exchange isolation of uranium from industrial solutions. Though it may seem strange, there are only a few papers published on this subject. Reference can be made to the paper of Disdar,[24] who applied ion exchange to the determination of traces of cadmium in uranium, and to Helger's paper[25] describing the ion exchange separation of uranium from sulfate and phosphate ions which interfere in the extraction of the metal.

Uranium is an amphoteric element but if we treat a uranium compound by any alkali, insoluble diuranates are precipitated. Thus, if we simply let a moderately acid solution, containing uranium and impurities, pass through a cationite in the hydrogen form, we may easily separate uranium from elements present in the solution as anions and, by a subsequent treatment of sorbent with alkali, separate it from such amphoteric elements as aluminium, vanadium, molybdenum, etc. The ability of elements to form complex compounds can be utilized for the separation of uranium from cations of non-amphoteric elements (iron, etc.). An experiment of this kind is mostly reduced to the absorption of ions by cationites first, and then to the selective desorption of uranium or impurities by the solution of a corresponding complex-forming compound.

One of the investigations (by Voskresenskaya) shows that when carbon ashes are treated with acid, uranium quantitatively dissolves; vanadium and molybdenum dissolve simultaneously, interfering in the weight and colorimetric determination of uranium. The suggested method of separating uranium from the impurities mentioned above was based on washing off the latter from the cationite column in the form of peracids. As a result of a number of experiments the author found that the dynamic capacity of paraphenolsulfonic cationite with respect to uranium from 0.144*N* solution of acid equalled 160 mg/gm; a further concentration of the solution led to a sharp decrease of the absorption value which made it possible to desorb uranium quantitatively (Fig. 3). The separation proceeded in the following way: after the absorption by the cationite of all cations from the given mixture and washing the column with water, a 5% solution of hydrogen peroxide was passed through it to elute vanadium and molybdenum. In order to remove the bubbles of oxygen from the column, the latter was washed with a stream of water from below and uranium was desorbed by 5% sulphuric acid. The amount of uranium in the effluent was found colorimetrically or by the weight method. The coincidence of the results of the chemical method and those of the chromato-

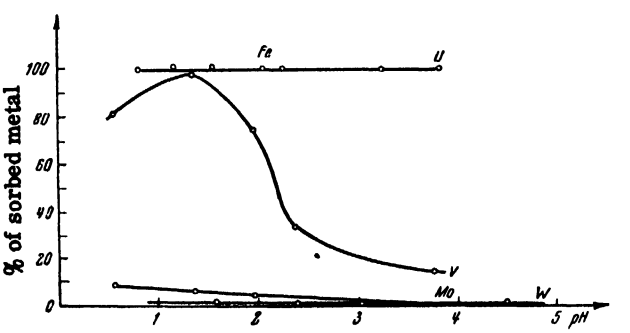

Figure 3. Influence of pH upon the absorption of uranium, molybdenum, vanadium, tungsten and iron (cationite KU-2 in the hydrogen form)

graphic method described above has provided a basis for the application of the latter method in analyses of carbon ashes on a large scale.

The principle of another method (suggested by Ryabchikov, Paley and Mikhailova) is that most of the elements associated with uranium form, in neutral or weak acidic media, stable complex compounds

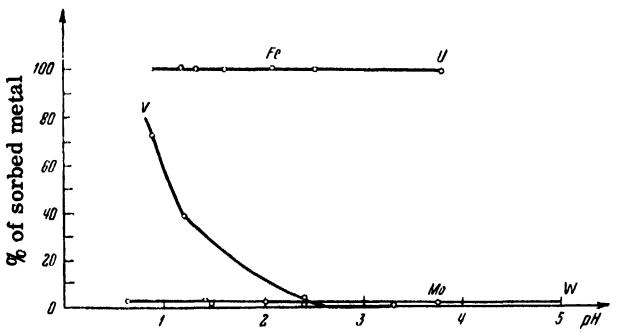

Figure 4. Influence of pH upon the absorption of uranium, molybdenum, vanadium, wolfram and iron (cationite KU-2 in the sodium form)

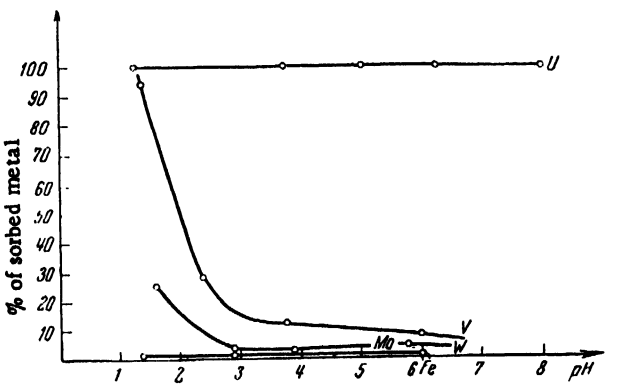

Figure 5. Influence of pH in the presence of EDTA upon uranium, molybdenum, vanadium, wolfram and iron (cationite KU-2 in a hydrogen form)

with salts of ethylenediamine tetra-acetic acid. After a thorough study of the absorption of uranyl and other ions by the cationite KU-2 in the presence and in the absence of EDTA (Figs. 3–6), the authors suggested the following method of separating uranium from iron, vanadium, molybdenum, tungsten, copper and lead. The disodium salt of EDTA (in a quantity equivalent to the approximate amount of uranium and impurity elements which may form complex compounds with the EDTA) was added to the solution to be analysed and the acidity of the solution was brought up to pH = 1.8–2.0; then the solution was passed through the column of the cationite KU-2 in the sodium form. All the above-mentioned impurities were eluted, while uranium, after washing the column with water was desorbed by a 10% solution of nitric or sulfuric acid. The effluent uranium was determined by the colorimetric and vanadometric methods. The suggested method was verified on a number of reference species and the results coincided fairly well with the standard data; this enabled the scientists to apply this method to the analysis of ores and various uranium-bearing materials.

Some investigations deal with the attempts to separate impurities from uranium using anionites, the impurity elements being absorbed in a complex anion from. Titov, Khalizova and Smirnova demonstrated a predominant (as compared with uranium) absorption by anionite MMG-1 (product of condensation of urea and melamine with guanidine) of iron from 3*N* hydrochloric acid; of vanadium from 0.5*M* solutions of oxalic or citric acids; of cerium from 0.5*M* solutions of oxalic acid with pH = 1.4. But quantitative separation was not achieved in any of those cases (Fig. 6).

Experiments in which complex-forming compounds were utilized for the selective elution of uranium from the cationate column represent a separate group. Ryabchikov, Senyavin, Mikhailova and Sarigina and later Klement[26] utilized ammonium carbonate which forms a stable complex with uranium. The experimental data on eluting uranium by ammonium carbonate from various types of cationites are given in Table I. The length of the column is 10 cm, the rate of the solution flow 1 cm/min.

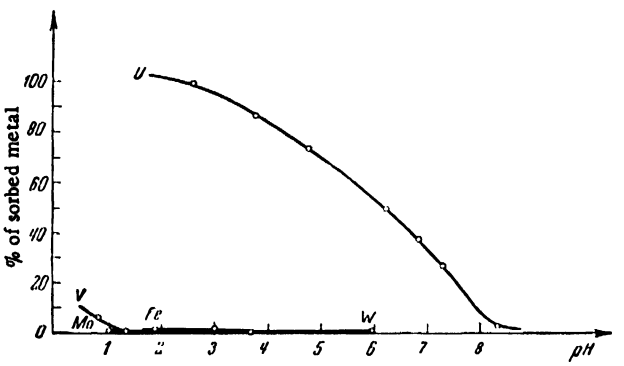

Figure 6. Influence of pH in the presence of EDTA upon uranium, molybdenum, vanadium, wolfram and iron (cationite KU-2 in a sodium form)

The principle of this method consists in eluting aluminium and vanadium from the column of cationite in the form of aluminate and vanadate with subsequent elution of uranium by ammonium carbonate. The solution under analysis with pH = 1.5–2.0 was filtered through the column of cationite in the hydrogen form, then the column was washed with distilled water and after that treated with a 10% solution of ammonia to elute aluminium and vanadium. This characterizes the specific nature of the chromatographic experiment as a dynamic experiment. The utilization of ammonia is more preferable as compared with alkalies because it can easily be freed from carbonates and possesses small replacing power owing to its low degree of dissociation. After the percolation of the column by alkali, a process which simultaneously neutralizes the hydrogen ions of the cationite, uranium was eluted by a hot 5%

solution of ammonium carbonate. The results of this method coincided fairly well with common chemical methods and this made it possible to recommend the chromatographic method for the determination of small amounts of uranium in ores, deposits and waste waters. In determining the amount of uranium in dilute solutions (in waste waters, for instance) by low-sensitivity methods it is recommended that a preliminary co-precipitation of uranium with iron hydroxide is carried out.

In the method described above, ammonium carbonate can be substituted by sodium fluoride (Khalizova and Smirnova). Uranyl ions form, as is known, stable, easily soluble, complex compounds with fluorine. At the same time, as the authors showed, sodium fluoride did not desorb iron from the cationite column, the column being previously treated with an ammonia solution. This fact enables the authors to apply this method to the analysis of solutions, containing large amounts of iron. In the effluent obtained, uranium was determined directly by the colorimetric method. The determination of the uranium in the reference samples by the above mentioned method made it possible to recommend it for analytical purposes.

Another change in the method described previously was suggested by Sobinyakova, Rubinstein and Maksheeva. Examining the process for eluting uranium from the column of the cationite KU-2 or MSF (product of condensation of paraphenolsulfonic acid with formaldehyde)—in the column treated previously with ammonia—the authors found that uranium in the form of a complex anion is desorbed selectively and in smaller volume by a 5% solution of ammonium acetate. It is essential that pH of the solution be 5.0–5.5, because a higher acid concentration leads to a desorption of iron, while a neutral medium causes a slow desorption of uranium.

Preliminary data have been obtained in a number of researches on the selective absorption of uranium by anionites, the metal being previously complexed. Investigations were also carried out on the absorption of uranium in dynamic conditions by various anionites from carbonate solutions, containing 0.74 gm/l of uranium; the results are given in Table II.

A simple and quick method was elaborated by Markov, Kharlamov and Medvedeva, which is based on the selective sorption of uranium by anionites and permits the rapid determination of uranium in natural water. In the latter, uranium is, as a rule, a component or uranyl carbonate anion complex and for its sorption the anionite MMG was utilized, previously converted into the bicarbonate form.

The determination proceeds as follows: the water under analysis was passed through the anionite bed; after filtration the resin was taken out from the column and placed into a glass where it was dissolved on heating in concentrated hydrochloric acid. In the solution obtained, the amount of uranium was determined by the fluorescent method. This method allows the determination of 0.020–0.002 mg/l of uranium to be carried out (with a relative error of ± 15%).

An attempt was made to separate chromatographically acetates of hexavalent uranium and thorium with the weakly basic anionite wofatit M (Nikolsky, Paramonova and Bjugina). Proceeding from the data obtained, the authors supposed that the external sphere of the complex contains thorium, because a further concentration of thorium acetate made the anionic-uranium acetate complex more stable.

The high effectiveness of the complex-forming compounds utilized in the chromatographic isolation of pure uranium requires a more detailed examination of their methods of application.

In this connection the synthesis of ion exchange resins capable of selectively absorbing either element from solutions of various compositions is of great interest.

Thorough investigations on the ways of synthesis of cationites for absorbing uranyl ions were made by Laskorin. Studying the absorption of uranyl ions by cationites with various functional groups, he found out that the presence of foreign salts has

Table I. Absorption of Uranium by Cationites and Its Desorption by Ammonium Carbonate*

Cationite name	*Functional group*	*Dynamic exchange capacity, mg/ml*	*Total dynamic exchange capacity, mg/ml*	*Volume of two per cent solution of ammonium carbonate used on eluting uranium, mg/ml*
KU-1	SO_3H; OH	90.8	97.6	750
KU-2	SO_3H	181.6	183.2	450
SBS	SO_3H	104.1	108.5	875
RF	PO_3OH	103.3	131.3	950
Wofatit C	COOH	13.3	30.9	750

* The table demonstrates that in the absorption of uranyl ions and their desorption by the ammonium carbonate solution, the cationite KU-2 gives the best results. Thus the cationite KU-2 was used in this research.

almost no influence on the capacity of selective cationites, whereas in 5% solution of sodium sulfate the capacity of the sulfocationite KU-2 in respect of uranium was practically nil, the capacity of another type of selective cationites under the same conditions decreased only from 80 to 50 mg/gm. This deviation from the elementary laws of ion exchange in the absorption of uranyl ions by selective cationites with an increase of their capacity when the temperature is raised, provided a basis for considering the absorption of uranyl ions as a chemisorption process of complex compound formation between uranyl ions and the functional groups which is also influenced by the nature and the degree of "crosslinking" of resin.

Possibilities to apply selective cationites for the separation of uranium from a number of elements during analytical determination were examined by Chekuleva and Makhmutova. Hydroxylamine hydrochloride was added to the solution under analysis

in order to completely reduce trivalent iron; then, by means of ammonia the solution was brought up to pH = 2.3–2.4 and was passed through the cationite column; after that the column was washed in water and rinsed with a 3% solution of hydrogen peroxide (for removing vanadium and molybdenum) and uranium was then eluted by sulfuric acid. In the effluent obtained, uranium was determined by the colorimetric or volumetric method. The method described above was verified by using solutions containing iron, molybdenum, vanadium, chromium, copper and nickel besides uranium and the results were quite satisfactory.

DISTRIBUTION CHROMATOGRAPHY

The separation of mixtures by the method of distribution chromatography is based, as is known, on the difference in the values of the distribution coefficients of substances between nonmixing "mobile" and "immobile" solvents. This difference is due to the ability of components to form complex compounds of various stability, almost undissociated and soluble in organic solvents. Uranium, unlike most associated elements, forms numerous complex compounds in such a ligand with the atoms of oxygen, sulphur, nitrogen and halogens. Nitrates are now widely used in experiments on the isolation of uranium by the method of distribution chromatography, because uranium forms acido-complexes, readily soluble in a number of organic solvents, particularly in diethyl ether. In this connection should be noted the papers[27, 28] on the separation of uranium from many elements by means of treating columns of paper pulp with ether, containing nitric acid.

The method of separation of uranium from impurities by utilizing silica gels was suggested by Markov. By using ammonia together with iron, aluminium, etc., uranium was precipitated from the solution obtained after fusion or after treating the material by acids; the precipitate was then dissolved in nitric acid and the solution was saturated with ammonium nitrate; pure large-pored silica gel was introduced into the solution obtained and after that it was transferred to the column, containing a saturated solution of ammonium nitrate in 0.5*N* nitric acid. Diethyl ether, previously equilibrated with the above-mentioned solution, is passed through the column. Uranium was determined in the effluent by volumetric or colorimetric methods.

RESULTS AND CONCLUSION

Some examples of the application of chromatography in analytical determination of uranium cited here show that ion exchange and distribution chromatography are simple and sufficiently adequate ways for isolating uranium from various solutions. The estimation of the parameters of the columns is made in accordance with the theory of the sorption dynamics, the foundation of which was laid by Shilov and Dubinin. Today Soviet and foreign researchers are successfully developing this theory.

Table II. Absorption of Uranium by Anionites

Anionite	*N-0*	*PE-9*	*N*	*TN*	*MM-2N*	*MMG-1*	*EDE10*
Absorption of uranium (per cent of initial amount of metal)	89	83.2	66.2	58.7	50.7	50.1	32.5

The choice of sorbents and conditions for experiment is mostly determined by specific chemical properties of uranium and impurity elements. In a simple variant, the separation of mixtures can be effected by a single passage of the solution with the sorbent in dynamic conditions. In ion exchange chromatography this thesis is confirmed by analyses which are based on amphoteric properties of the impurity elements as well as on the ability of these elements or of uranium to form complex compounds. The application of cationites, selectively absorbing uranium, seems to be extremely promising. The ability of uranium to form various complex compounds with functional groups of cationites is also important for the synthesis of cationites.

The meagre data published so far on the chromatographic isolation of uranium makes it impossible to appreciate the comparative effectiveness of the methods described above. It should be noted, however, that these methods ensure the separation of uranium from practically all impurities that interfere in the determination of the element and consequently can be successfully applied to the analysis of ores, waste waters and other materials containing uranium.

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Paper Chromatographic Separation of Uranium in Natural Resources

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The separation of uranium from other elements, by paper chromatography, was performed in order to determine uranium in natural resources. The content of uranium was found to be from 0.005–0.15%.

The determination of uranium was carried out by the fluorophotometric method. It was found that under the conditions of the fluorescence of uranium, cerium salts also fluoresce, equivalent to a content of 0.3% of uranium in cerium salts.

When separating very small quantities of uranium (5×10^{-9} gm of U), it was established that the fluorescence of cerium is not due to the presence of uranium. In the fluorophotometric determination of uranium it is necessary to separate cerium, because it interferes with the analysis of uranium and causes incorrect results.

The separation of uranium from other elements, for the purpose of determination, has mainly been carried out by different extraction methods.[1, 2] Besides, some use has been made lately, of the chromatographic separation methods either of the method of cellulose columns [3-5] or paper chromatography.[6, 7]

The solvents used in the chromatographic separation of uranium are usually the same as those applied as extraction solvents for the uranium separation. The best results are obtained when the selective solubility of uranium in a given solvent is high, and the partition coefficient of the cations present, in the solvent-water system, small.

Uranium was first qualitatively separated from Fe, Ni, Co, Cr, Pb, Cu, Bi, V, Ti, Zr, Eu, Ce, Th, Hg, Cd, Al, Ca, Ba and Mg, by several extraction solvents. These accompanying elements were in form of nitrates, in a 5% HNO_3 solution. Whatman filter paper No. 3 MM was used. The following solvents were found to be convenient for the separation of uranium from these elements: (1) 80% (v/v) isobutyl methyl ketone + 20% HNO_3 (1.40); (2) 80% butyl acetate + 20% HNO_3; (3) 90% di-*n*-butyl ether, 2% tri-*n*-butyl-phosphate + 8% HNO_3: Iso-butyl methyl ketone and HNO_3 have been used as solvents by Hahofer and Hecht for the chromatography of uranium previously separated by ether extraction.[7]

When using the first two solvents, uranium is located on the solvent front of the 16 cm chromatogram (Fig. 1 *a, c* and *d*); whereas with the third solvent it is much more spread out (Fig. 1 *b*). All other elements are found on the starting line or slightly above, with exception of thorium which is spread over the paper. Thorium can be stopped by addition of Na_2HPO_4 or H_3PO_4 to the solution (Fig. 1 *d*).

The solvent containing 80% of iso-butyl methyl ketone and 20% HNO_3 was found the most convenient and has been used in most of our work.

SEPARATION OF URANIUM

After the separation of uranium from the accompanying elements was investigated qualitatively, a quantitative analysis was done. Uranium was separated in concentrations of $1.6 \times 10^{-4} - 5 \times 10^{-9}$ gm.

The method of Williams and Kirby[8] was applied, with an upward run of the solvent, on Whatman No. 3 MM paper. The solution was placed in drops, with a micropipette of 0.1 ml on a 2×21 cm strip of Whatman paper, 2.5 cm from the bottom. Each drop was separately dried under an infra red lamp.

After the chromatogram was developed, it was dried and the part with the uranium spot cut out. When the uranium concentrations were low, the cut out strip was burned and heated in a platinum dish in which the determination was carried out. After adding NaF, the mixture was fused and uranium determined fluorimetrically. At high concentrations of uranium the cut out strip was burned and heated in a platinum crucible, dissolved in HNO_3, then diluted to a definite volume and uranium determined by colorimetric or fluorimetric method. Results are given in Table I.

As is evident from Table I, the separation of uranium from the elements cited is quantitative within the given concentration range of uranium. Even in the presence of SO_4^{--}, Cl^-, and PO_4^{---} the separation of uranium is quantitative, which is not the case when it is carried out by ether extraction[1, 2] or by chromatography with cellulose columns.[3-5]

DETERMINATION OF URANIUM

Colorimetric Determination

Ammonium thioglycolate was used as reagent.[9] The method permitted a determination of uranium in concentrations to 4×10^{-6} gm/ml.

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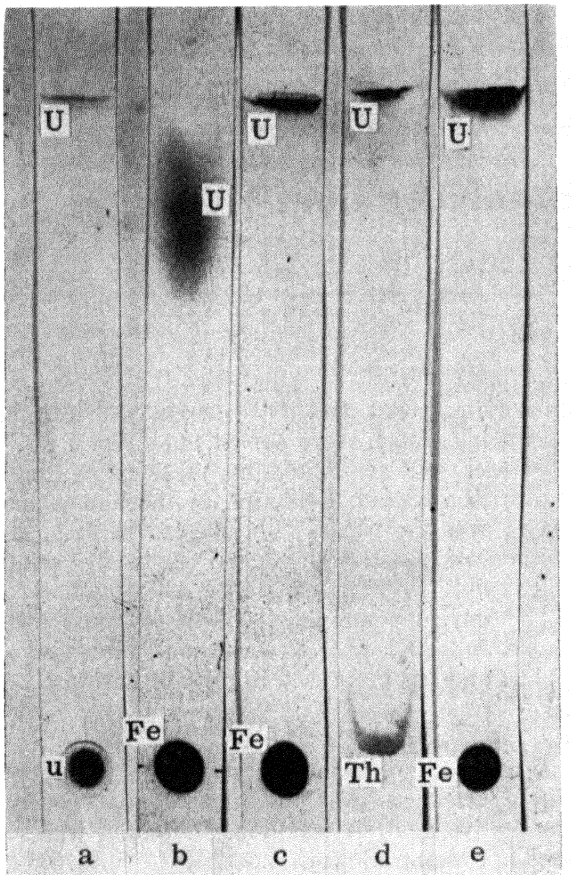

Figure 1. (a) Cerium and uranium separation by 80% iso-butyl methyl ketone + 20% HNO_3; (b) Iron and uranium separation by 90% di-n-butyl ether, 2% tri-n-butyl phosphate + 8% HNO_3; (c) Separation of Fe and U by 80% iso-butyl methyl ketone + 20% HNO_3; (d) Separation of Th and U by 80% iso-butyl methyl ketone + 20% HNO_3; thorium was stopped by addition of Na_2HPO_4 to the solution; (e) Separation of Fe and U by 80% butyl acetate + 20% HNO_3

Experiments were done on the Zeiss electrophotometer Elko II with a S 38 E filter (380 mμ).

Fluorimetric Determination

Uranium has mostly been determined by the fluorimetric method, based on the fluorescence of uranium fused with sodium fluoride and the irradiation of the melt with ultra-violet rays. The sensitivity of this method is very high and permits a determination of uranium to 10^{-10} gm.[10, 11] However, four other elements have been reported to give fluorescence when fused in sodium fluoride. They are: Nb, Nd, Er and Ce(II). Because of the very weak fluorescence intensity of these elements (2×10^{-4} gm of Er produces fluorescence of the same intensity as 4×10^{-9} gm of U), they do not disturb the determination of uranium, with the exception of cerium. In his experiments with cerium compounds, Simpson[12] found a fluorescence equivalent to 0.2–0.9% U in cerium. Zimmerman[13] mentions the necessity of separating uranium from cerium, because of the fluorescence of cerium, which interferes with the fluorophotometric determination of uranium.

The instrument used for the determination of uranium was a photo-electric fluorimeter, constructed in the Institute "Boris Kidrich," of a type similar to that described by Price *et al.*[10] The sensitivity of the instrument was 10^{-9} gm U.

CHROMATOGRAPHIC SEPARATION OF URANIUM FROM CERIUM AND FLUORIMETRIC DETERMINATION OF THESE ELEMENTS

When melting cerium salts with sodium fluoride, it was found that the melted substance emits fluorescence of an intensity which would correspond to 0.3% of uranium in cerium. Because of the possibility

Table I

Elements present, gm	*Quantity of U in gm after separation by paper chromatography*	
	Fluorimetric determination	*Colorimetric determination*
1.6×10^{-4} U 3×10^{-3} Fe 5×10^{-4} Ti 2×10^{-4} V 1×10^{-4} Pb, Cu, Co		$(1.60 \pm 0.04)\times10^{-4}$
4×10^{-5} U 1×10^{-4} Fe 1×10^{-5} V, Ti, Zr, Ce, Cu, Pb, Ni, Cd, Ba, Mg	$(3.89 \pm 0.14)\times10^{-5}$	$(4.1 \pm 0.2)\times10^{-5}$
4×10^{-6} U 1×10^{-5} Fe 1×10^{-6} V, Ti, Zr, Ce, Cu, Pb, Ni, Cd, Ba, Mg	$(4.05 \pm 0.21)\times10^{-6}$	
8×10^{-6} U 1.2×10^{-5} Th 2×10^{-5} Fe 2×10^{-6} Vi, Ti, Zr, Ce, Cu, Pb, Ni, Cd, Mg 4.8×10^{-4} SO_4'' 3×10^{-5} PO_4''' 3.5×10^{-4} Cl'	$(7.80 \pm 0.27)\times10^{-6}$	
8×10^{-9} U 1.2×10^{-5} Th 8×10^{-5} Fe 2×10^{-6} V, Ti, Zr, Ce, Cu, Pb, Ni, Cd, Mg 4.8×10^{-4} SO_4'' 3.5×10^{-4} Cl' 3×10^{-5} PO_4'''	$(7.6 \pm 0.4)\times10^{-9}$	
1×10^{-8} U 4.8×10^{-4} SO_4'' 3.5×10^{-4} Cl' 3×10^{-5} PO_4'''	$(9.94 \pm 0.11)\times10^{-8}$	

Table II

U and Ce present, gm	U found fluorimetrically, without previous separation, gm	Excess of U due to fluorescence of Ce, %	U found fluorimetrically after chromatographic separation, gm	Ce found fluorimetrically after chromatographic separation, gm
1×10^{-7} U 3.7×10^{-5} Ce	$(0.99 \pm 0.06)\times10^{-7}$		$(0.95 \pm 0.04)\times10^{-7}$	$(3.2 \pm 0.4)\times10^{-5}$
1×10^{-7} U 3.7×10^{-6} Ce	$(1.10 \pm 0.04)\times10^{-7}$	10	$(0.96 \pm 0.05)\times10^{-7}$	$(3.8 \pm 0.6)\times10^{-6}$
1×10^{-8} U 3.7×10^{-6} Ce	$(2.0 \pm 0.2)\times10^{-8}$	100	$(0.97 \pm 0.08)\times10^{-8}$	$(3.7 \pm 0.4)\times10^{-6}$
5×10^{-9} U 3.7×10^{-6} Ce	$(1.6 \pm 0.1)\times10^{-8}$	220	$(4.8 \pm 0.5)\times10^{-9}$	$(3.2 \pm 0.2)\times10^{-6}$

that the fluorescence of cerium is due to very small amounts of uranium present in cerium, as assumed by Price *et al.* for niobium and neodymium, chromatographic separation of small quantities of uranium from cerium was carried out as well as an analysis of cerium solutions.

After the separation of uranium from cerium, both elements were determined in the same manner. The cerium spot on the chromatogram was cut off, then burned and heated in a platinum dish, used in fluorimetry. It was melted with sodium fluoride and the fluorescence measured on the fluorimeter. The results are shown in Tables II and III.

The values of uranium determined from the fluorescence intensity of melted uranium and cerium in sodium fluoride, in a given concentration range, are shown in the second column of Tables II and III.

It can be seen that the yield of uranium is increased owing to the fluorescence of cerium. For this reason, cerium had first to be separated. A similar increase in uranium yield, due to the fluorescence of cerium, is also found in cases when uranium and cerium are melted with other elements.

The possibility that the fluorescence of cerium is brought about by small quantities of uranium which might be present in cerium was rejected, as uranium has been separated and fluorimetrically determined in quantities corresponding to less than 0.3% of uranium in cerium. (Fluorescence of 3.7×10^{-6} gm of Ce corresponds to a fluorescence of 1×10^{-8} gm of U; 5×10^{-9} gm of U was separated from 3.7×10^{-6} gm of Ce.) Besides, both uranium and cerium were determined fluorimetrically after separation, cerium showing greater deviations owing to its uneven distribution in sodium fluoride.

LIST OF REAGENTS USED

Iso-butyl methyl ketone (B.D.H. Laboratory Reagent, London)

Tri-*n*-butyl phosphate (Bios Laboratories, Inc., New York)

Di-*n*-butyl ether (Bios Laboratories, Inc., New York)

Butyl acetate (Riedel-de Haën A. G., Seelze b.Hannover)

These solvents were first distilled, then dried over corresponding drying agents and redistilled. Tri-*n*-butyl phosphate was distilled under reduced pressure.

HNO_3 p.a. (E. Merck, Darmstadt)

HCl A.R. (Mallinckrodt Chemical Works, St. Louis-New York-Montreal)

H_2SO_4 A.R. (Mallinckrodt Chemical Works, St. Louis-New York-Montreal)

$Ce(SO_4)_2 \cdot 4H_2O$ p.a. (E. Merck, Darmstadt)

$Ce(NO_3)_3 \cdot 6H_2O$ puriss. (E. Merck, Darmstadt)

NaF p.a. (Prolabo, Rhône-Poulenc)

Table III

Elements present, gm	U found fluorimetrically, gm: Without previous separation	Excess of U, due to fluorescence of Ce, %	After chromatographic separation
1×10^{-7} U, 3.7×10^{-5} Ce, 1×10^{-7} Mn, Fe, Co, Cu, Cd	$(1.20 \pm 0.07)\times10^{-7}$	20	$(0.95 \pm 0.02)\times10^{-7}$
1×10^{-8} U, 3.7×10^{-6} Ce, 1×10^{-7} Mn, Fe, Co, Cu, 4.5×10^{-7} Cd	$(2.0 \pm 0.1)\times10^{-8}$	100	$(0.98 \pm 0.05)\times10^{-8}$
1×10^{-8} U, 3.7×10^{-6} Ce, 2×10^{-7} Mn, Fe, Co, Cu, 9×10^{-7} Cd	$(2.5 \pm 0.2)\times10^{-8}$	150	$(0.96 \pm 0.05)\times10^{-8}$
5×10^{-9} U, 3.7×10^{-6} Ce, 1×10^{-7} Mn, Fe, Co, Cu 4.5×10^{-7} Cd	$(2.0 \pm 0.2)\times10^{-8}$	300	$(5.1 \pm 0.5)\times10^{-9}$
3.7×10^{-6} Ce 1×10^{-7} Mn, Fe, Co, Cu, 4.5×10^{-7} Cd	$(1.2 \pm 0.2)\times10^{-8}$		

Table IV

Ores	*Fluorimetric determination without previous separation, gm U/tonne*	*Colorimetric determination after separation by cellulose columns method, gm U/tonne*	*Fluorimetric determination after separation by paper chromatography, gm U/tonne*
Schist 1	1440 ± 70	1480 ± 50	1465 ± 60
Silicate ore	875 ± 43	920 ± 15	850 ± 40
Ash of coal	422 ± 20	407 ± 10	399 ± 24
Schist 2	128 ± 5	129 ± 12	136 ± 11
Schist 3	44 ± 4		45 ± 6

Chemicals of E. Merck and Riedel-de Haën p.a. or puriss., were used for the preparation of other reagent solutions.

SEPARATION OF URANIUM FROM ORES

Uranium was determined in schists, silicate ores and coal, containing 0.005–0.15% of U. Ores were dissolved in the usual way with HNO_3 + HF. Hydrofluoric acid was then driven off by HNO_3. The final solution to be applied in the chromatographic separation contained about 5% of HNO_3.

The solution containing 0.1–1 gm of ore was then diluted to a convenient volume and uranium determined as described above. Five chromatograms were made of each solution. After the development, one of them was treated with a $K_4Fe(CN)_6$ solution. If a qualitative reaction on uranium was obtained, the spot was cut out and burned and heated in a platinum crucible, then dissolved in nitric acid and diluted to a convenient volume. In case that $K_4Fe(CN)_6$ gave no reaction of uranium, the uranium spot on chromatogram strip was cut out, burned and heated in the platinum dish for the fluorimetric determination. Sodium fluoride was added and after melting, uranium determined by the fluorimetric method. This procedure permits the determination of 5×10^{-4}% of U, with an error of 10–15% in solutions containing 1 gm of ore, diluted to 100 ml.

Table IV gives the values of uranium content of five different ores, as determined after the separation by paper chromatography. These values are compared to those obtained by cellulose column chromatography as well as to those obtained, without previous separation, by the "spiking" method.[11]

As seen in Table IV, paper chromatography was found to be a satisfactory method for the separation of uranium, to be determined in ores containing up to 0.005% of uranium. Another advantage of this method in comparison with the ether extraction or the cellulose column method, is that the sulfates, chlorides and phosphates do not interfere.

ACKNOWLEDGEMENTS

The authors are indebted to Professor P. Savić for his constant interest and valuable suggestions in the course of this work. Thanks are also due to Mrs. V. Dokić for help in preparing the ores.

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Effect of Petroleum Ether on the Separation of Uranium in Low Grade Samples when Using Cellulose Columns

By D. Lebez and M. Ostanek,* Yugoslavia

Chromatographic separation of uranium from other cations in cellulose columns by Burstall and Wells[1] has shown good results at concentrations of uranium down to 10^{-2}%, when applied either to synthetic samples or to minerals. At lower concentrations (10^{-3}–10^{-4}% range) the recovery of uranium was unsatisfactory. As the solubility of the aqueous and solvent phases in each other is relatively high when ether containing 5 vol % of nitric acid is used as solvent, it was suspected that there is some breaking through of the aqueous phase resulting in quenching of the fluorescence in sodium fluoride, especially when large volumes of the sample solution had to be adsorbed on the cellulose. On the other hand it is probable that in these unfavourable conditions the solubility of the solvent in the aqueous phase contributes to incomplete elution of uranium.

Therefore it was hoped that it might be possible to extend the applicability of the method to extremely poor ores by changing the composition of the solvent.

EXPERIMENTS

In the original procedure uranium is separated from the mineral sample as follows: the cellulose powder must be treated with the solution of the sample containing 25 vol % nitric acid. The amount required for 10 ml of this solution is 2 gm of cellulose. The sample thus treated is transferred into the column whereupon 150 ml of the solvent are allowed to flow through it.

In preparing the mineral sample the original method was followed. The further procedure was carried out in this manner: first the cellulose powder was saturated with ether containing 5 vol % nitric acid; ether was then evaporated on a water-jet pump; the cellulose thus dried was used immediately. The composition of the solvent was changed to contain: 20 ml of petroleum ether; 190 ml of ether and 10 ml of nitric acid (sp.gr. 1.42). For the columns of 25 to 30 cm in height and of 10 to 20 mm in diameter 100 to 200 ml of the solvent were used. The way of transfer of the sample into the column is determined by the quantity of the sample solution. 10 ml portions were transferred directly to the top of the column. The treatment of the cellulose powder with portions of larger volumes (up to 40 ml) was carried out separately on cellulose prepared in the manner as described above. The pulp was then transferred into the column containing a 5–10 cm high column of cellulose powder soaked with the solvent.

When all the solvent had been passed through the column the uranium was stripped into the aqueous phase by shaking the solution in the separatory funnel three times with 10 ml of 1*N* sulphuric acid according to the method used in our laboratory.[2] Owing to the low quantity of uranium only the fluorimetric determination could be used. The aqueous solution was evaporated to a small volume and fluorimetric discs containing 0.2 to 1.2 μg U_3O_8 were prepared from appropriate aliquots of the solution.

RESULTS

In Table I results of the analysis of siliceous ore by using the original method are shown. Though there exists a tolerable accordance between the tabulated values and the results obtained by the extraction method[2] the tendency towards the lower results is evident. With samples containing 1×10^{-3}% U_3O_8 the chromatographic results were essentially lower than those obtained by extraction. On the other hand it is evident from Tables II and III that 90% elution was obtained by addition of petroleum ether to ether although the quantity of uranium was very low. In Tables IV, V and VI, results for siliceous ores are shown.

DISCUSSION

The experiments in which ether containing 5 vol % nitric acid was used, have shown that with the samples containing very small quantities of uranium lower results are obtained by the chromatographic method than by ethyl acetate extraction. We were not able to transfer more than 10 ml of the sample solution into the column (height 30 cm, diameter 20 mm). As soon as the quantity of the solution applied had been further increased, the aqueous phase and with it the other cations broke through the column. By adding petroleum ether to the organic phase the relation between the hydrophobic properties of the organic solvent on the one hand, and the hydrophilic properties of the cellulose on the other, increases to such an extent that it is possible, at the same quantity of the cellulose, to transfer almost three to four times larger volumes of the sample without the aqueous phase breaking through the column. At the same time the solubility of the ura-

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Table I. Sample 2308-A (Siliceous Ore)*

The chromatographic separation: *Fluorimeter* μg	U_3O_8 *in the sample* %
0.93	0.0045
0.95	0.0046
0.90	0.0043
0.92	0.0044
0.92	0.0044

* Height of column: 30 cm; diameter of column: 20 mm; composition of solvent: ether containing 5 vol % nitric acid; quantity of solvent: 100 ml; 10 ml of the sample solution containing 25 vol % nitric acid was transferred to the top of the column.

The extraction method has shown the following results (fluorimeter): 0.99 μg (0.005% U_3O_8).

Table II. Synthetic Sample*

The chromatographic separation: *Fluorimeter* μg
1.12
0.95
1.08
1.12
1.05
1.10
1.13

* Height of column: 25 cm; diameter of column: 20 mm; composition of solvent: ether containing 5 vol % nitric acid and 9 vol% petroleum ether; quantity of solvent: 220 ml; 25 ml of the sample solution containing 25 vol % nitric acid was transferred to the top of the column.

Theoretic value (fluorimeter):
1.15 μg (6.9×10^{-4}% U_3O_8).

Table III. Synthetic Sample*

The chromatographic separation: *Fluorimeter* μg
0.155
0.165
0.175
0.180

* Height of column: 30 cm; diameter of column: 20 mm; composition of solvent: ether containing 5 vol % nitric acid and 9 vol % petroleum ether; quantity of solvent: 220 ml; 40 ml of the sample solution containing 25 vol % nitric acid was transferred to the top of the column.

Theoretic value (fluorimeter):
0.184 μg (9.8×10^{-5}% U_3O_8).

nium in the solvent was high enough to make the quantitative recoveries of uranium possible. Due to the circumstances thus changed, the results mentioned above for the synthetic samples containing 6.9×10^{-4} and 9.8×10^{-5} per cent U_3O_8 approach the theoretical values to a considerable extent. Moreover, with some low-grade ores we obtained even higher values than by the extraction method.

The advantage of the proposed solvent, when the chromatographic method is to be applied, can especially be seen from the results shown in Table III. In these tests, 40 ml of the solution of the synthetic

Table IV. Sample 2277-A (Siliceous Ore)*

The chromatographic separation: *Fluorimeter* μg	U_3O_8 *in the sample* %
1.22	0.0015
1.12	0.0014
1.30	0.0016
1.20	0.0015
1.12	0.0014
1.08	0.0013

* Height of column: 30 cm; diameter of column: 20 mm; composition of solvent: ether containing 5 vol % nitric acid and 9 vol % petroleum ether; quantity of solvent: 220 ml; 25 ml of sample solution containing 10 vol % nitric acid was transferred to the top of the column.

The extraction method has given the following results (fluorimeter): 0.96 μg (0.0012% U_3O_8).

Table V. Sample 1045 (Siliceous Ore)*

The chromatographic separation: *Fluorimeter* μg	U_3O_8 *in the sample* %
1.40	0.0017
1.02	0.0013
1.03	0.0013

* Height of column: 30 cm; diameter of column: 20 mm; composition of solvent: ether containing 5 vol % nitric acid and 9 vol % petroleum ether; quantity of solvent: 220 ml; 25 ml of sample solution containing 10 vol % nitric acid was transferred to the top of the column.

The extraction method has shown the following results (fluorimeter): 0.88 μg (0.0011% U_3O_8).

Table VI. Sample 1131 (Siliceous Ore)*

The chromatographic separation: *Fluorimeter* μg	U_3O_8 *in the sample* %
0.90	0.0011
0.80	0.0010
0.75	0.00094
0.75	0.00094

* Height of column: 30 cm; diameter of column: 20 mm; composition of solvent: ether containing 5 vol % nitric acid and 9 vol % petroleum ether; quantity of solvent: 220 ml; 25 ml of sample solution containing 10 vol % nitric acid was transferred to the top of the column.

The extraction method has shown the following results (fluorimeter): 0.80 μg (0.0010% U_3O_8).

sample, containing 4.6 μg U_3O_8, were transferred into the column. The results obtained by thorough treatment approached the theoretical value to as high as 84% or even up to 90%. The new solvent composition extends considerably the applicability of the column chromatographic method and simplifies the technique by making it possible for appreciable quantities of aqueous phase to be directly transferred into the column.

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The Use of Ion Exchange Resins for the Determination of Uranium in Ores and Solutions

By Sallie Fisher and Robert Kunin,* USA

The routine analysis of uranium in relatively pure solutions at all concentrations has been well worked out through the cooperation of a number of laboratories.[3] Likewise the analysis of complex materials wherein uranium is a minor constituent has been thoroughly developed following the classical methods of analytical chemistry. These methods, while yielding excellent results of high accuracy, are far too time and space consuming for the laboratory analysis of large numbers of uranium samples per day. In cases where quantity is equal in importance to quality, the fluorimetric method of analysis[1, 2] has proved valuable for samples of very low uranium content. This method has not, however, proved sufficiently accurate for impure samples of moderate to high uranium content. The need for a rapid, routine method for samples in this higher concentration range prompted the present work.

It was known at the onset that certain anion exchanging resins would absorb the anionic uranium(VI) sulfate complex. As many of the ions that interfere in the quantitative determination of uranium are cationic, the use of such a resin for an analytical separation of uranium was considered. The method outlined here was developed from this idea, modified by several years' experience with the routine analysis of uranium in solutions containing known and unknown interfering ions.

APPARATUS

The resin columns used in this work were one-half and one inch diameter glass tubes with a high porosity glass filtering disc fused to the lower end. Equally successful columns may be improvised from ordinary burettes using a small glass wool plug to retain the resin. Flow rate of liquids through the resin bed was regulated by either a stopcock or screw clamp. A separatory funnel attached to the top of the column by means of a rubber stopper was used as a vessel for the introduction of samples and reagents to the column.

REAGENTS

Except for the resin, reagent grade chemicals were used in the procedure without further purification. The resin was a quaternary ammonium type, Amberlite IRA-400. A 40–60 mesh (U.S. screens) size was used in these experiments. The resin was pretreated with three volumes of 10% sulfuric acid and rinsed free of excess acid to a methyl red endpoint with deionized or distilled water. This treatment may be performed in the columns where the resin is to be used. However, if a large number of samples are analyzed per day it is more convenient to prepare the resin in large batches. Fresh resin must be used for each determination.

PROCEDURE

Opening of Ores

A number of procedures for the opening of uranium-bearing ores were tried in an attempt to find a rapid method compatible with the ion exchange separation procedure. Of those, two have given satisfactory results in the opening of a wide range of ore types. The first of these is the standard opening technique[1] wherein the ore is treated with a 1–2 mixture of nitric and hydrofluoric acids and evaporated to dryness, repeatedly if necessary. The dry residue is subsequently fused with sodium carbonate. The cooled melt is flooded with water and dissolved by the addition of sulfuric acid. The solution so obtained may be used directly in the ion exchange separation procedure.

A second method for the opening of ores has proved satisfactory where speed and simplicity of operation and apparatus are of prime importance. Here the ore is mixed with approximately one-half its weight of manganese dioxide. Sufficient 10% sulfuric acid is added to produce a fluid mixture. This acidic mixture is heated to boiling and then set aside to cool to room temperature. The cooled sample is diluted with two to three volumes of water and filtered through fine-pored paper to remove the excess manganese dioxide and the ore residue. The filtrate is used for the ion exchange separation and analysis of uranium.

Ion Exchange Separation

If the material to be analyzed is a solution suspected of containing major amounts of chloride or nitrate the sample must be evaporated to fumes with sulfuric acid and rediluted with water prior to the ion exchange separation. In the case of samples containing no sulfate, sufficient sulfuric acid or sodium sulfate should be added to provide at least 2 grams of sulfate ion per liter. All samples, whether original-

* Rohm & Haas Company, Philadelphia, Pennsylvania.
Including work by J. Benson, D. Kenny and A. Preuss.

Table I. Uranium Recovery with and without Sulfurous Acid

Added ion mg/sample	*Added H_2SO_3 ml/sample*	*Recovery of uranium, %*
none	0	101
none	10	100
390 Fe(III)	0	204
390 Fe(III)	10	113
390 Fe(III)	20	103
390 Fe(III)	30	100
27.6 V(V)	0	100
33.6 V(V)	20	100
69.0 V(V)	0	61.2
138 V(V)	0	24.1
134 V(V)	30	102
100 Mo(VI)	0	101
100 Mo(VI) + 100 Fe(III)	10	81.8
100 Mo(VI) + 100 Fe(III)	30	99.3

ly solutions or the product of the opening of an ore, should be partially neutralized with sodium or potassium hydroxide to a residual acidity of less than 0.1 gram ion per liter prior to the separation. The resultant solution is further treated with an excess of 6% sulfurous acid to reduce certain interfering ions such as iron(III) and vanadium(V) to their lower valence states. The decolorization of methylene blue may be used as an indicator for this step. Large excesses of sulfurous acid have not interfered in the subsequent separation.

The solution so prepared is passed through a column of Amberlite IRA-400 at a moderate rate of flow. The ratio of solution to resin and the dimensions of the column may be varied according to the uranium content of the solution to be analyzed. Since the resin will concentrate as well as separate uranium, large volumes of very dilute solutions may be used as the sample. Following the absorption of uranium by the resin, the column is washed with a small amount of water to remove the last traces of interfering cations. The uranium is subsequently eluted with dilute perchloric acid. In the present study the uranium content of the perchloric acid effluent was determined colorimetrically using the standard sodium hydroxide-hydrogen peroxide method.[1] Higher concentrations of uranium could also be analyzed by the standard oxidation-reduction techniques[3] using a zinc reductor and cerate titration.

INTERFERING IONS

Materials which would interfere in the ion exchange separation of uranium are of two types. First there are ions which will compete with the uranium for resin sites and hence which may cause loss of the uranium into the sample effluent. The second type are ions also retained by the resin and subsequently eluted to interfere in the analysis. Potentially, all anions give interference of the first type. Of the common anions, nitrate ($> 0.01N$) and chloride ($> 0.1N$) gave the most serious interference as shown by uranium losses to the sample effluent. Sulfate ($< 0.5M$) and phosphate up to concentrations where precipitated uranium did not interfere.

Interference of anions retained by the column and subsequently eluted with the uranium was eliminated by the sulfurous acid treatment. Typical analyses showing the effect of this reduction are given in Table I. All variables, such as sample volume, uranium content, resin volume, flow rate, and the volume and concentration of the eluting agent, were held constant in these experiments. Only the concentration of the added ion and of the sulfurous acid were varied. These results indicate that the magnitude of the interference is a function of the nature and amount of the ion added but that it can be completely eliminated by pre-reduction of the sample. However, the results also indicate that this reduction must be complete before the interference is eliminated.

No error arising from the presence of materials that are normally cationic under the conditions of the experiment has been noted. Among the ions tested are aluminum, calcium, magnesium, manganese(II), cobalt, copper and iron(II), either alone or in combination with each other.

TYPICAL RESULTS

The method was tested on a series of ores, previously analyzed at the New Brunswick Laboratories of the United States Atomic Energy Commission using the standard cupferron separation of uranium followed by colorimetric estimation.[1] Samples for the ion exchange separation were opened both by the nitric-hydrofluoric acid fuming followed by sodium carbonate fusion and by the manganese dioxide–sulfuric acid oxidative leaching procedure. Reduction with sulfurous acid was followed by ion exchange separation in both cases. The uranium content of the perchloric acid eluent was determined colorimetrically. Duplicate samples were used where sufficient ore was available. The analyst had no knowledge of the nature of the ores except that their uranium content would probably be low. Results (Table II) by the ion exchange method are

Table II. Analyses of Ores by Different Methods

		Per cent U_3O_8		
			Ion exchange	
Ore	*Type*	*Standard separation**	*I†*	*II‡*
A	Pitchblende (?)	0.41	0.39	0.34
B	Carnotite	0.34	0.31	0.32
C	Fe, Al silicate	0.05	0.020	0.035
D	Carnotite	0.68	0.65	0.73
E	Phosphate	0.029	0.025	0.067, 0.052
F	Pitchblende	3.36	3.31	3.35, 3.39
G	Carnotite	0.18	0.19	0.20, 0.18
H	Carnotite	0.11	0.11	0.14, 0.11

* Results of New Brunswick Laboratory, standard method.
† Ore opened with HF-HNO_3 and Na_2CO_3.
‡ Ore opened with MnO_2-H_2SO_4.

in close agreement with those obtained by the cupferron separation.

Under average conditions an analyst can handle 10–12 solid samples at one time, and with the manganese dioxide leaching technique, should be able to analyze two such sets per day. Where the uranium is already in solution, 40 aliquots may be analyzed per day by a single analyst if no fuming is required and the uranium is estimated colorimetrically. In the analysis of solutions an accuracy of $\pm 2\%$ of the uranium content in the sample is expected. Experience with ores in this laboratory is not sufficient to permit a critical evaluation of the accuracy of the results. However, results where the uranium content is 0.1% or greater have always been in good agreement with the results obtained by standard methods.

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Strychnine Uranyl Fluoride: A New Uranium Compound Suitable for the Determination of Fluorine and of Uranium in Presence of Some Other Metals

By A. Riad Tourky and A. M. Amin,* Egypt

The gravimetric determination of fluorine as calcium fluoride[1] or as lead chlorofluoride[2] is still beset with difficulties. The proposed procedures are often tedious and comprise many inconveniences. They are mostly based on the formation of precipitates possessing appreciable solubility and which are difficult to filter due to their gelatinous character.

Previous work done in this laboratory has shown that of the double fluorides formed with uranium, potassium and more particularly strychnine, form difficultly soluble compounds. In addition to being crystalline, easy to filter, strychnine uranyl fluoride, which has been prepared for the first time, has the advantage of possessing a high molecular weight, and a conversion factor for fluorine lower than in any other known insoluble fluorine compound. We have studied the possibility of applying this compound for the determination of fluorine.

If to a solution containing fluorine, uranyl and strychnine salt solutions are added, there is the possibility, in addition to the formation of strychnine uranyl fluoride, that uranyl hydroxide and/or strychnine base may be precipitated. Since strychnine uranyl fluoride was found to be stable in fairly acid solution, it was deemed necessary to determine the pH below which none of the above ingredients is liable to be precipitated.

TITRATION OF URANYL NITRATE WITH POTASSIUM HYDROXIDE

Curve *A* in Fig. 1 represents the titration of a uranyl nitrate solution with potassium hydroxide. The solution whose initial pH value was 3.1 remained clear till 1.4 equivalents of alkali hydroxide were added, at which point the solution became opalescent and attained a pH value of 4.29. Precipitation was then complete when 2.3 equivalents of the alkali hydroxide were added.

Since two rather than three equivalents of the alkali hydroxide are required for precipitation, it is plausible to assume that the hydroxide and not the uranate is formed. The circumstances that the excess quantity of alkali hydroxide is constant and that the region of precipitation is not parallel to the x axis, suggests that a process of condensation involving oxygen bridge formation and splitting of hydrogen ions occurs whereby the hydrogen ions released neutralize part of the alkali hydroxide added.

pH OF PRECIPITATION OF STRYCHNINE BASE

Strychnine sulphate (Analar grade) was dissolved in carbon dioxide-free redistilled water to make a 0.01 molar solution; 4 ml of 0.1N sulphuric acid per 100 ml were added to repress hydrolysis. The titration was performed potentiometrically using 0.1N potassium hydroxide. The representative titration curve *B* shown in Fig. 1 reveals that the initial pH value amounting to 2.2 increases steadily till about pH 7 when it runs horizontally till about 20 ml are added. This corresponds to the precipitation of the base, which requires 10 ml of alkali hydroxide as compared with 21 ml used. The excess is apparently adsorbed by the freshly formed base.

TITRATION OF A MIXTURE OF STRYCHNINE SULPHATE AND URANYL NITRATE WITH POTASSIUM HYDROXIDE

Since we shall use a mixed solution of strychnine sulphate and uranyl nitrate in the present investigation to serve as a reagent for the determination of fluorine in soluble fluorides, the titration of the mixture with alkali hydroxide has been made in the same manner as in the foregoing experiments. For this purpose a mixed solution 0.002 and 0.001M with respect to uranyl nitrate and strychnine sulphate respectively was slightly acidified with hydrochloric acid so as to become 0.0015M with respect to this acid to suppress hydrolysis. The result of titration of this mixture with 0.2N potassium hydroxide is shown in Fig. 2. The curve shows that the precipitation of both uranyl hydroxide and strychnine base takes place at practically the same pH values as the separate solutions. The completion of precipitation of the strychnine base was found, however, to take place at a somewhat higher pH (7.86 instead of 7.0).

The conclusion which may be drawn from the foregoing experiments is that in order to precipitate strychnine uranyl fluoride without co-precipitation of either uranyl hydroxide or strychnine base, the pH of the solution should not exceed 4.

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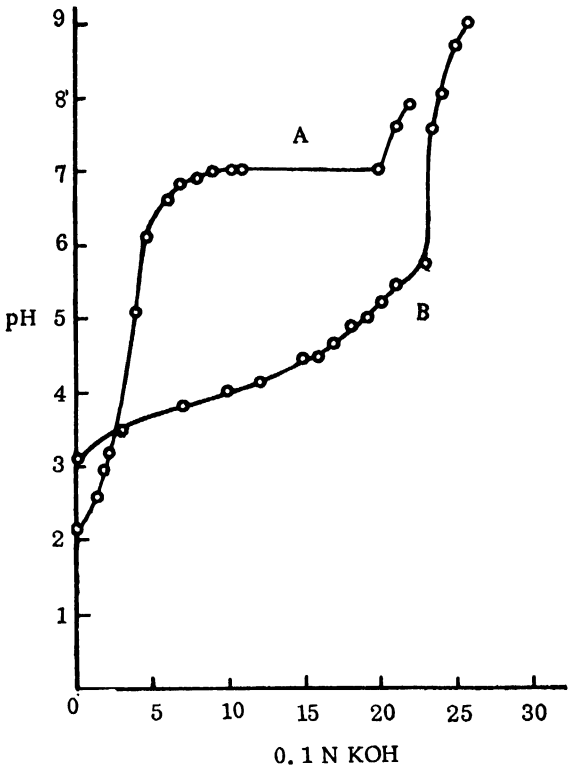

Figure 1. (A) Titration of uranyl nitrate with 0.1N alkali; (B) titration of strychnine sulfate with 0.01N alkali

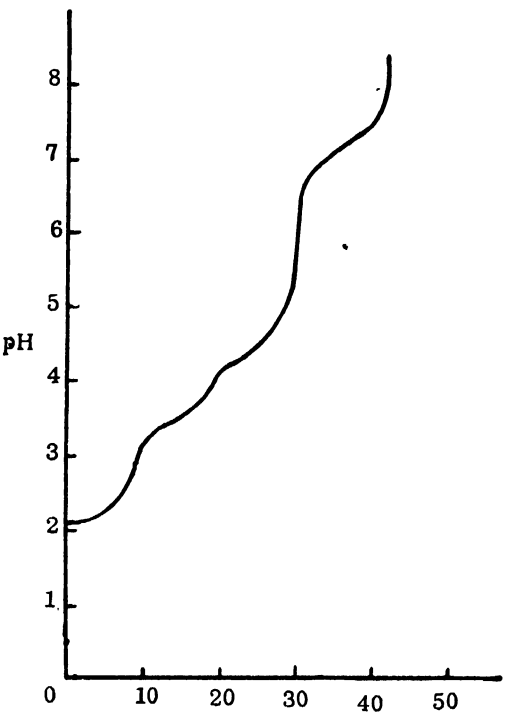

Figure 2. Titration of uranyl nitrate and strychnine sulphate with KOH

pH OF PRECIPITATION OF STRYCHNINE URANYL FLUORIDE

The next step involved the determination of the pH range within which strychnine uranyl fluoride precipitates and whether the reaction can be completed before uranyl hydroxide begins to precipitate. Since a potassium fluoride solution possesses an alkaline reaction, the titration can be performed using this reagent. A mixed solution 0.04 and 0.02*M* with respect to uranyl nitrate and strychnine respectively, the acidity of which was adjusted at a pH value ranging from 1.5 to 2, was titrated with 0.04*M* potassium fluoride solution. The curve in Fig. 3 shows that the initial pH value of 1.62 increases but slowly till 76 ml of the reagent are added, whereby the pH value attained amounts to 2.19. The curve shows that precipitation is complete at about pH 2.12. This pH lies before that at which either uranyl hydroxide or strychnine base precipitates out. The same picture was obtained on titrating solutions of pH values 1.25, 1.88 and 2.02 in which the volumes of fluoride solution required amounted to 24, 28, and 9.1 ml respectively, which compare satisfactorily with the theoretical values 24, 27.4 and 9.09 ml.

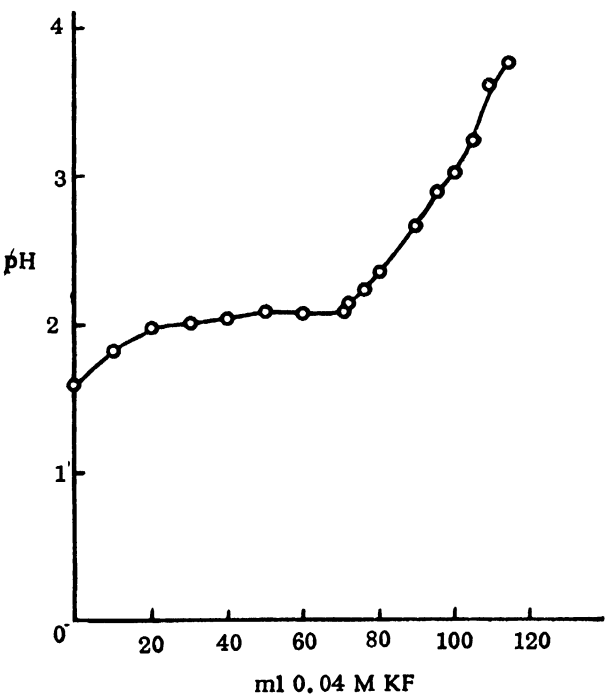

Figure 3. Titration of reagent with KF

It was now deemed desirable to use an acetic-acetate buffer to control the pH value of the solution mixture. The pH value of a mixture with the ratio 9:1 is 3.6 which is still too acid to cause the precipitation of uranyl hydroxide. By applying this buffer with the proposed reagent mixture consisting of 0.04*M* uranyl nitrate and 0.2*M* strychnine sulphate, it was found that the mixture remained optically clear during the experimental period covering the time one month.

In order to make certain that in the above buffer mixture of pH 3.6 no precipitation of uranyl hydrox-

Table I. Composition of the Precipitate Formed at Different pH Values

p H	*Carbon* %	*Hydrogen* %	*Nitrogen* %	*Residue* %
1.89	40.27	3.80	4.67	38.86
2.09	40.31	3.79	4.20	38.25
2.54	40.45	3.80	3.87	38.74
3.04	40.05	3.89	4.39	39.21
3.65	40.64	4.12	4.56	38.18
4.00	40.37	4.03	4.62	38.97
4.02	40.51	4.06	4.44	38.38
4.19	39.90	3.92	4.43	39.20
4.35	40.40	4.24	4.36	39.56
4.91	39.30	3.92	4.76	40.90
5.04	39.23	4.17	4.22	41.56
5.18	39.30	4.17	4.10	41.88
5.60	40.14	3.50	4.15	50.18
6.00	7.65	0.95	nil	98.11

ide takes place, a series of precipitations were performed within the wide pH range of 1.89 to 6. The pH values of the solution were adjusted either by the addition of acid or alkali as required after the addition of potassium fluoride solution. The precipitates were left to stand for two days, filtered through sintered glass crucibles, washed with 60% ethyl alcohol and dried at 100°C in vacuum till constant weight. Samples of each preparation were microanalysed for their carbon, hydrogen, nitrogen and the residue assumed to consist of U_3O_8. The results of these analyses (Table 1) show that the precipitates formed between pH 1.89 and 4.19 possess practically the same composition, whereas at higher pH values up to 6 a gradual rise of the residue manifests itself, indicating co-precipitation of uranyl hydroxide. These data show that in precipitating pure strychnine uranyl fluoride the pH of the solution should not exceed 4.

COMPOSITION OF THE PRECIPITATE FORMED

A series of precipitations were made under uniform conditions at one and the same pH of about 3.5. The buffered reagent consisting of 30 gm glacial acetic acid and 5.45 gm sodium acetate, 17.12 gm of strychnine sulphate and 20.087 gm of uranyl nitrate was prepared by dissolving these ingredients in redistilled water and the solution diluted up to 1 liter in order to become 0.04*M* with respect to uranyl nitrate and 0.02*M* with respect to strychnine sulphate. The solution remained optically clear for one month and its pH value was constant.

The reagent was added in excess in platinum dishes to portions of potassium fluoride containing 25 mgm of fluorine (in 25 ml). The precipitates formed were filtered after two days standing, washed with 60% alcohol, dried in vacuum and microanalysed. The results of representative analysis are given in Table II. Based on analytical data the composition of the precipitate was found to correspond to the empirical formula:

$$7(C_{21}H_{22}O_2N_2HF)\cdot 6(UO_2F_2)\cdot 2HF$$

The above formula is based on the premise that the residual ash consists only of U_3O_8. A liable error may arise from the residue not having exactly the above composition or from contamination with potassium carbonate. Although potassium could not be detected analytically in the residue, spectroscopic examination revealed very faint lines characteristic of this element. One could avoid the occlusion of any trace of potassium on precipitating strychnine uranyl fluoride by admixing together in a platinum dish uranyl fluoride and strychnine base dissolved in a slight excess of hydrofluoric acid. The precipitate formed in a series of 11 experiments yielded on analysis practically the same results.

In the above determinations the fluorine content of the precipitates was evaluated by difference. This may be subject to some error if a small quantity of water was occluded, which could not be reproducibly removed. In a series of experiments direct determinations were therefore made by adding the reagents to a known excess of a potassium fluoride solution, allowing the precipitate to stand for 3 days at room temperature, filtering, washing, drying at 100°C and weighing. The amount of fluorine was determined in the filtrate volumetrically, using thorium nitrate as reagent and sodium alzarin sulphonate as the indicator following the procedure recommended by Rowly and Churchill.[3] By subtraction from the amount originally present, the fluorine content of the precipitate could be calculated. The results of a series of 10 determinations are shown in Table III.

From these results it can be seen that the fluorine amounts to 9.142% as compared with the average values of 9.132 and 9.039% as determined by difference, confirming thus the empirical formula given for strychnine uranyl fluoride.

EFFECT OF TIME AND CONCENTRATION ON THE COMPLETION OF PRECIPITATION

The effect of time and concentration on the completion of precipitation were traced by adding con-

Table II. Results of Micro-Analysis of Precipitates Formed at pH 3 from the Reagent and Potassium Fluoride and from Admixing Uranyl Fluoride and Strychnine Base in Excess Hydrofluoric Acid in Aqueous Solution

	From reagent and potassium fluoride	*From UO_2F_2 and strychnine in HF*	*Theory*
Carbon	40.46	40.48	40
Hydrogen	3.95_6	3.93_1	
Nitrogen	4.45_2	4.32	
UO_2	37.04_4	37.14	
Strychnine	53.61_4	53.62_1	53.54
H to from strychnine (calc.)	0.15_0	0.15_0	0.16
Uranyl radical	37.04_4	37.14_0	37.11
Fluorine by diff.	9.14_2	9.03_9	9.14
H in HF (calc.)	0.05_0	0.05_0	0.05
Total	100.00	100.00	100.00

Table III. Determination of Fluorine Content in the Precipitate

Precipitate, mg.	1165.0	1168.0	1166.2	582.7
Fluorine, mg.	106.67	106.63	106.57	53.24
Found, %	9.15_6	9.12_9	9.12_8	9.13_7
Precipitate, mg.	583.1	388.6	382.9	291.4
Fluorine, mg.	53.29	35.53	35.02	26.73
Found, %	9.14_0	9.14_0	9.14_1	9.16_7
Precipitate, mg.	291.5	116.6	—	
Fluorine, mg.	26.65	10.64	—	
Found, %	9.14_0	9.12_6	—	
Average	Nil	Nil	9.14_2	

stant volumes of the buffered reagent to known amounts of freshly ignited potassium fluoride. The solutions were kept in a thermostat at 30°C ±0.2° for different periods of time, filtered at different intervals and washed with 60% alcohol saturated with the same precipitate, so as to prevent dissolution of the precipitate. The precipitate was then dried and weighed. The total volume in each experiment amounted to 100 ml after addition of reagent.

Five sets of experiments were made. The fluorine ion concentrations in these experiments were 60, 80, 100, 150 and 180 mg/100 ml. The data represented in Fig. 4 reveal that at the minimum concentration of 60 mg fluorine per 100 ml, the time required for the maximum amount of precipitate to be formed under

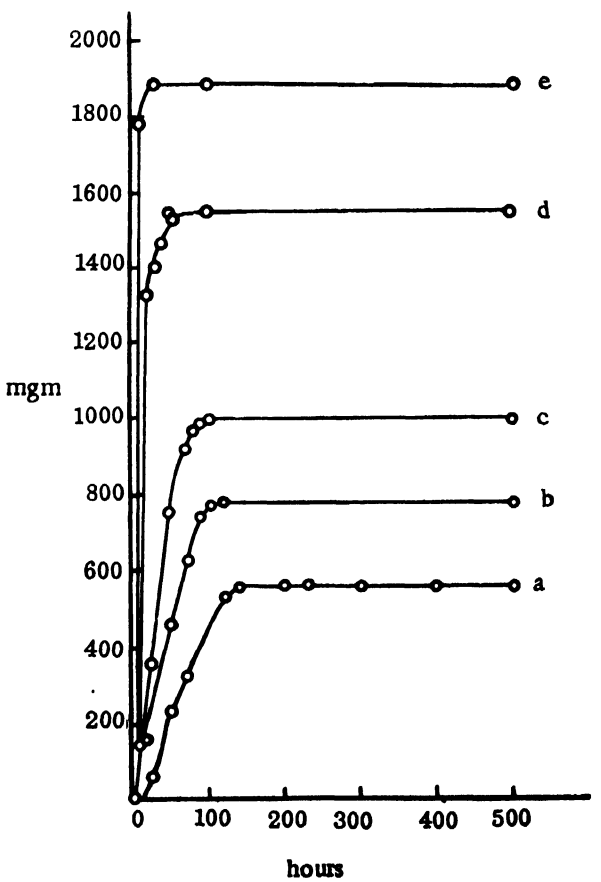

Figure 4

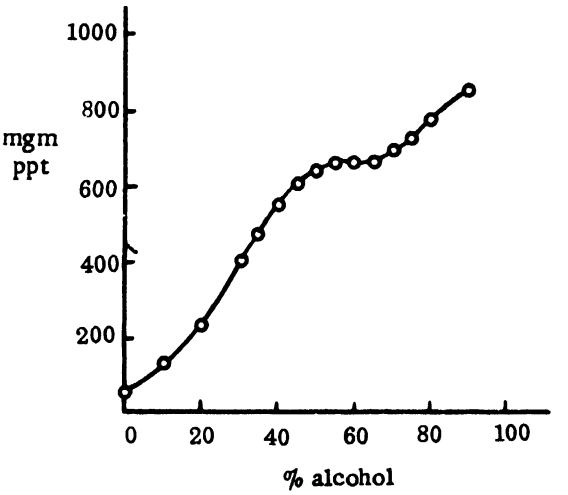

Figure 5

these conditions amounts to 134 hr. As the fluorine concentration increases the time required decreases and the percentage amount of precipitate formed increases. The data show that for the quantitative precipitation of fluorine under the above conditions, either a correction factor of 0.0829 mg of fluorine per ml of solution is to be applied or that the process is to be modified so as to render the precipitation more quantitative.

PRECIPITATION FROM WATER-ALCOHOL MIXTURES

It was tried to find out whether water-alcohol mixtures could be more advantageously used for precipitation than pure water.

As is shown in Fig. 5, the amount of precipitate increases continuously with increase of the proportion of alcohol present up to 50%. At concentrations of alcohol higher than 70%, the amount of precipitate increases at first rapidly and then slowly. Table IV shows that the precipitates formed in 0–70% alcohol solutions have uniform composition and correspond to the aforementioned formula. At higher alcohol concentrations the composition of the precipitate deviates, apparently due to contamination with other ingredients. We have chosen a 60% alcoholic solution as the most suitable precipitating medium.

Table IV. Analysis of Precipitate Formed in Different Alcohol Concentrations

	%	%	%	%	%	%
Alcohol	0	2	5	10	15	20
Uranyl radical	36.75	37.11	36.61	36.86	36.82	36.61
Strychnine	53.07	53.23	53.53	53.15	53.71	53.53
Alcohol	30	40	50	60	65	70
Uranyl radical	36.98	36.96	37.15	38.44	38.17	37.33
Strychnine	54.06	53.40	53.61	54.06	53.24	53.39
Alcohol	75	80	85	90	95	
Uranyl radical	39.35	40.30	40.33	80.47	80.46	
Strychnine	53.00	49.67	49.18	10.72	8.52	

In such a solution, the presence of potassium up to 70 mg/100 ml does not interfere in the precipitation of the compound.

ACCURACY AND PRECISION OF THE METHOD

The results of experiments carried out to determine the accuracy and precision of the method for the determination of fluorine (Table V) show that no precipitation takes place when the fluorine concentration lies below 0.33 mg per ml. Above this limit increasing amounts precipitate out up to a concentration of 1.6 mg of fluorine per ml, when the fluorine found in the precipitate amounted to 99.95% of the amount initially present. Higher concentrations of fluorine give results of the same order of accuracy. From the given data the standard error of the determination of fluorine in 60% alcohol solution was calculated and found to amount to ± 0.04%.

THE DETERMINATION OF URANIUM IN PRESENCE OF SOME OTHER METALS

The low solubility of strychnine uranyl fluoride in water and in 60% alcohol at 25°C amounting to 47.5 mg and 30 mg/100 ml respectively at pH 3.5 permits the determinations of uranium in the presence of a number of cations such as Zn^{++}, Sn^{++}, Sn^{++++}, Sb^{+++}, Bi^{+++}, Cr^{+++}, Fe^{++}, Ce^{++} and Ni^{++}, the fluorides of which are either soluble or much more soluble than the compound.

Details concerning this separation will be published elsewhere.

Table V. Accuracy and Precision of Fluorine Determination by Precipitation in 60% Alcohol*

Fluorine concentration mg/ml	*Present mg*	*Fluorine*		
		Found mg	*Difference mg*	*%*
0.127	6.44	0.00	- 6.44	-100.00
0.256	12.82	0.00	-12.82	-100.00
0.336	17.32	3.22	-14.10	- 81.41
0.400	20.07	8.36	-11.71	- 58.35
0.614	32.19	24.60	- 7.59	- 23.58
0.757	6.44	5.89	- 0.55	- 8.54
1.038	27.26	26.45	- 0.81	- 2.97
1.237	10.94	10.91	- 0.03	- 0.27
1.235	32.73	32.47	- 0.26	- 0.79
1.276	70.82	70.69	- 0.13	- 0.18
1.423	38.18	38.20	0.02	0.05
1.600	19.53	19.52	- 0.01	- 0.05
1.616	43.63	43.60	- 0.03	- 0.07
1.800	19.53	19.54	0.01	0.05
2.00	19.53	19.54	0.01	0.05
4.00	19.53	19.50	- 0.03	- 0.15

* Standard error $= \pm \sqrt{\Sigma d^2/(n(n-1))}$ where d = deviation from true value, and n is the number of determinations. Standard error of the last seven determinations = ± 0.04%.

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Separation of Alkali Metals and Alkaline-Earth Metals from Uranium and Their Determination by Flame Spectrophotometry

By Julia F. Possidoni de Albinati and Jorge H. Capaccioli,* Argentina

Alkali metals and alkaline-earth metals found as impurities in uranium or its compounds can be easily and rapidly determined by extraction from this element and their analysis by flame spectrophotometry. Thus, a single operation can yield the results which otherwise would require special methods for each particular element.

The limits of sensitivity established by us for the measurement of these metals appear in Table I.

The method under study is based on these data, and its accuracy is subject to the sensitivity of the apparatus.

REAGENTS AND INSTRUMENTS

Nitric acid, free from rare earths and alkaline metals, is prepared by distillation of the chemically pure acid in a quartz vessel. The purified product is kept in a quartz or "Vycor" container. The purity test is made by evaporating 30 ml in a quartz or platinum crucible, dissolving the residue with redistilled water and measuring the elements in a flame spectrophotometer.

Water used is redistilled, using quartz vessels.

Ethyl ether, alcohol free. Shake one liter of ether in a separation funnel with 4 or 5 lots of redistilled water, 200 ml each, decanting the aqueous layer each time.

Li, Na, K, Rb, Cs, Ca, Sr and Be in standard solutions. The standard solutions, kept in polyethylene containers, contain 1 mg/ml of metal in the nitrate form. The dilute solutions are prepared immediately before use since glass volumetric apparatus may be employed if contact with the solutions is short (a few hours).

Quartz still. All water used during the process is produced in a "Heraeus" still.

Flame spectrophotometer. The Beckman DU spectrophotometer was used with flame attachment (No. 9200); oxyacetylene burner (No. 4030); phototube (No. 157) special for flame (625–1000 mμ range); phototube No. 2342-1 was used for the blue region.

Decanting ampules, quartz.

Volumetric material. 10, 5, 2, 1 and 0.1 ml graduated and recalibrated pipettes. 25 ml graduated beakers; 5 ml graduated containers.

Glasses and capsules, quartz.

Quartz still for nitric acid.

SPECTRA OF ALKALI METALS AND ALKALINE-EARTH METALS

Figures 1 to 8 show the emission spectrum of the elements of interest. The abscissae are the wavelengths (millimicrons) and the ordinates are the luminous intensities read on the transmittance scale of the apparatus (*"%T"*). The concentrations of the elements and the corresponding slit widths are given for each case.

Sodium, lithium, potassium and calcium give a single well-defined peak. Rubidium gives one maximum and two secondary peaks, one of which interferes with the optimum wave of potassium. Cesium displays two peaks; the lesser one may interfere with the readings for barium. Strontium has one principal and one secondary peak which should be taken into account during the determination of small amounts of lithium. Calcium, although it gives a single maximum peak, produces luminosity in a wide range of wavelengths, and may create difficulties for the estimation of small amounts of sodium. Finally barium is the most unfavorable case: the low intensity of its emission is combined with weak luminosity over a wide range of wavelengths.

CALIBRATION CURVES

Calibration curves were constructed to check on the linear correlation betwen concentrations and luminous intensities, the effect of the interfering element being studied in each case. Figures 9 to 16 represent these curves.

Table II is based on the results obtained with known concentrations of alkali metals and alkaline-earth metals, measured at the wavelengths shown and with the slits used relative to the respective elements.

ANALYTICAL APPLICATION

Since the calibration functions give straight lines when the concentrations are plotted vs luminosities, the concentration of an unknown sample can be computed mathematically from the graph of readings

Original language: Spanish.

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of a solution of known concentration and the readings for distilled water.

This method eliminates the errors due to reference ("dark") current changes during a series of readings and the errors caused by changes in the sensitivity of the apparatus.

The effect of interfering elements may be also disregarded in each case, by taking the readings at the proper wavelengths.

Some synthetic samples analyzed by this method, yielded good results. Following are some examples (note the lower limits of detection, which are subtracted from the calibration curves).

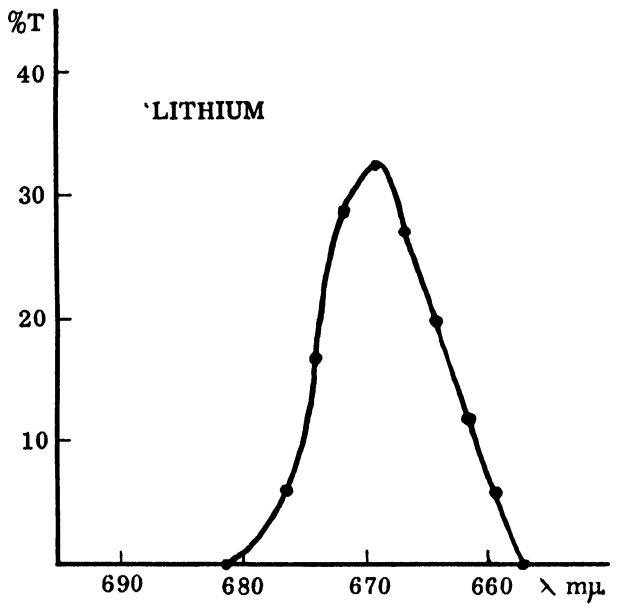

Figure 1

Table I

Element	Concentration limits
Lithium	10^{-7}
Sodium	10^{-6}
Potassium	10^{-5}
Rubidium	10^{-5}
Cesium	10^{-5}
Calcium	10^{-5}
Strontium	10^{-5}
Barium	10^{-4}

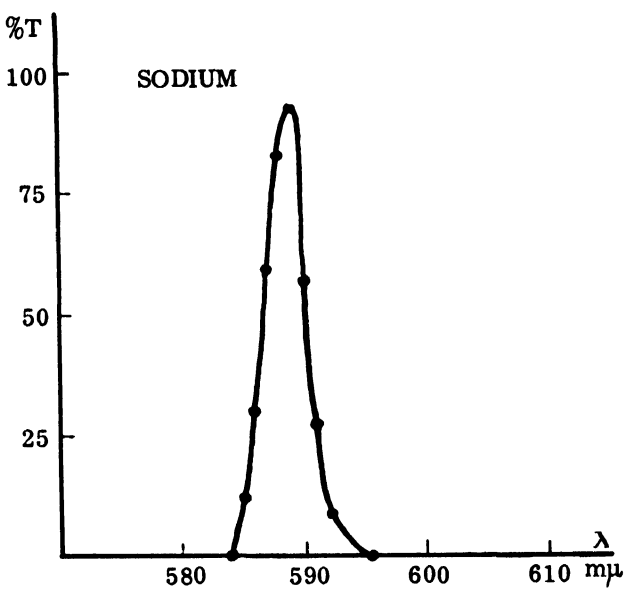

Figure 2

Sample 1

Element	True concentration (γ/ml)	Measured concentration (γ/ml)
Ca	45	45
Na	110	110
Li	4	4
Sr	40	50
K	15	17
Rb	6	7
Cs	0	1
Ba	10	..

Sample 2

Element	True concentration (γ/ml)	Measured concentration (γ/ml)
Ca	100	95
Li	8	8
Sr	0	0
K	20	22
Cs	40	40
Ba	80	100

Sample 3

Element	True concentration (γ/ml)	Measured concentration (γ/ml)
Ca	8	9
Na	0	0
Li	0.3	0.5
Rb	4	5

SEPARATION OF URANIUM

Uranium may be separated by precipitation as uranium tetrafluoride by electrolytic reduction of uranyl sulfate in hydrofluoric acid, using a platinum plate as the cathode and a coil of the same metal as the anode:[1]

$$UO_2(SO_4) + 2H_2SO_4 \rightarrow U(SO_4)_2 + 2H_2O + SO_4^{=}$$

$$U(SO_4)_2 + 2HF \rightarrow H_2[U(SO_4)_2F_2]$$

$$2H_2[U(SO_4)_2F_2] \rightarrow UF_4 + U(SO_4)_2 + 2H_2SO_4$$

The separation is achieved more readily by ether extraction. Uranium nitrate is extractable by several organic solvents, particularly ketones and ethers.[2-6] One of the most frequently used is ethyl ether. The highest efficiency is obtained if the aqueous phase is saturated with ammonium nitrate and the acidity raised to 1.5*M* with nitric acid. Under these conditions, the extraction coefficient reaches to 3.5.

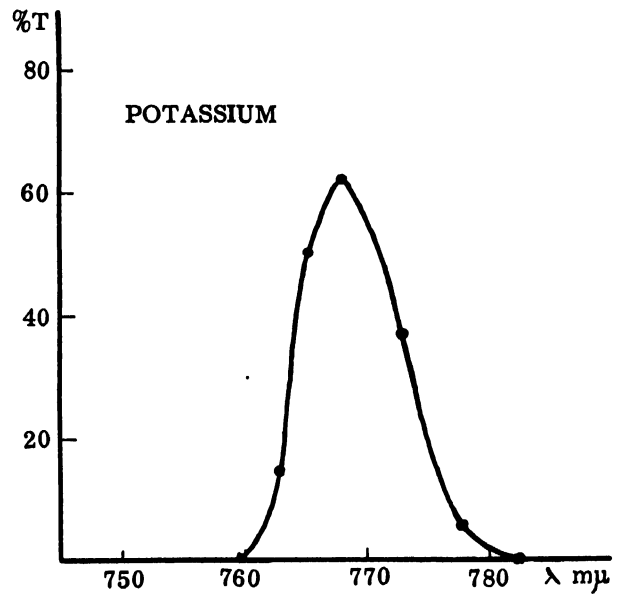

Figure 3

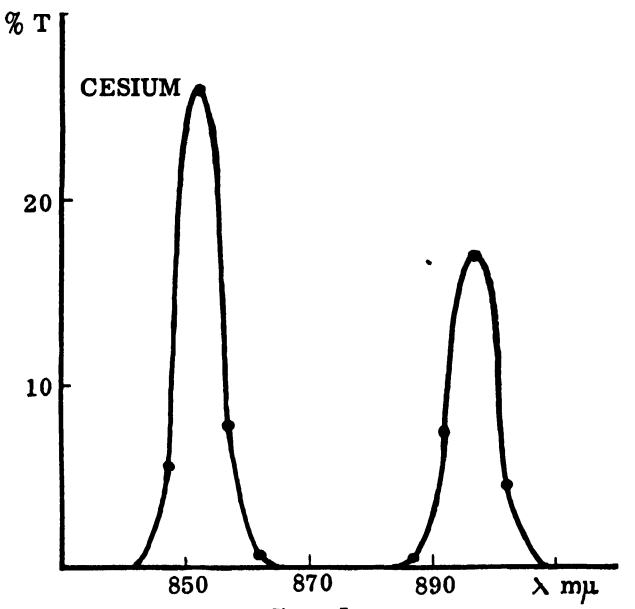

Figure 5

However, in the absence of ammonium nitrate in the aqueous phase, the optimum concentration of nitric acid is 4–5*M* and then the coefficient is 2.3.[7]

The extraction coefficient is the ratio applicable to all the species of the same substance in the two phases. Conversely, the distribution coefficient applies strictly to the concentration ratio of a given species between the non-miscible solvents in equilibrium.[8] Since uranyl nitrate passes generally to the ether with four molecules of water of hydration[2] and to the aqueous phase with six, reference is made to the extraction coefficient found while studying extraction with this solvent.

The optimum working conditions in this case were obtained experimentally. Ammonium nitrate was not used since it made it difficult to carry out the estimation of the elements in the aqueous phase. The volume of water is maintained at about 5–8 ml; a larger volume would hinder the extraction and lengthen the duration of the next stage of the analytical work. On the other hand, handling is difficult with smaller aqueous-phase volumes. Nitric acid is added to the measured volume of water before each extraction, since the acid is distributed throughout the water and the ether, and its concentration decreases in the former. In each extraction, 20 ml of ether are used. If these precautions are taken, 5 or 6 extractions are sufficient to eliminate up to 10 gm of uranium.

RECOVERY OF ALKALI METALS AND ALKALINE-EARTH METALS ADDED TO THE URANIUM

Use is made of uranyl nitrate assumed to be free from alkali metals and alkaline-earth metals, since it has been previously extracted with ether. The

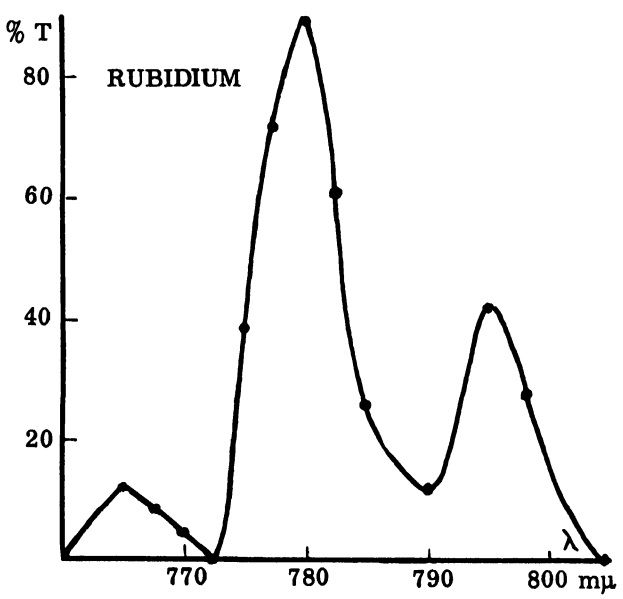

Figure 4

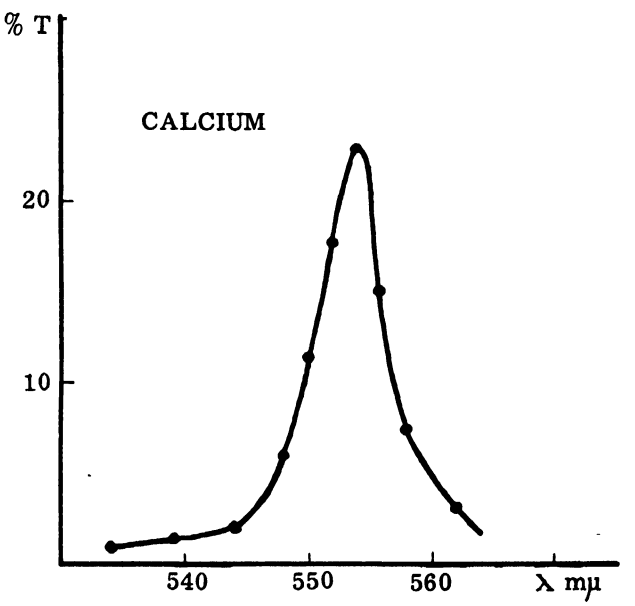

Figure 6

Table II. Values Obtained on the Flame Spectrophotometer with Typical Solutions

Element and conc. in γ/ml	λ	554	589	671	681	768	780	852	873
	"slit"	0.33	0.10	0.18	0.17	0.05	0.10	0.20	0.20
Ca (100)		58	14	0	0	0	0	0	0
Na (100)		0	307	0	0	0	0	0	0
Li (100)		0	3	485	0	0	0	0	0
Li (10)		0	0	76	0	0	0	0	0
Sr (100)		0	0	8	9	0	0	0	0
K (100)		0	0	0	0	73	3	0	0
Rb (100)		0	0	0	0	4	95	0	0
Cs (100)		0	0	0	0	0	0	106	1
Ba (500)		0	0	1	0	0	0	11	17

solvent is evaporated, and portions are taken, equivalent to 6 gm $UO_2(NO_3)_2 \cdot 6H_2O$.

Known amounts of the elements to be recovered are added to these portions. Extraction is carried out and each residue is determined by comparing it with a standard solution of equal concentration. Table III shows the results.

The results are sufficiently close to justify the claim that the method yields an efficient separation of the alkali metals and alkaline-earth metals from uranium.

Table III

Element	Observed concentration (γ/ml)	
	Aqueous residue obtained by extraction of uranium with nitric acid and ether	Standard aqueous solutions
Ca	85	80
Na	19	20
Li	2	2
Sr	100	100
K	23	25
Rb	40	40
Cs	9	9
Ba	300	300

PROCESS USED

Separation of Uranium

The extraction process should be applied to uranyl nitrate. If the sample is uranium metal, UO_3 or U_3O_8, it should be dissolved in previously distilled nitric acid and evaporated just to dryness. The crystals are transferred to a quartz separating funnel (amount to be treated: 6 gm uranium or its equivalent in oxide or nitrate). About 5 ml redistilled water, 4 ml nitric acid and 20 ml alcohol free ether are added. The mixture is stirred vigorously, allowed to separate, and a new extraction is made. Extraction is repeated, until the ether and aqueous layers are colorless.

The aqueous phase is transferred to a quartz flask, in which the washings from the separation funnel are recovered. These liquids are boiled, in order to eliminate the small amount of ether remaining in the aqueous layer and to reduce the volume to about 3 ml. The liquid is cooled and transferred to a 5 ml

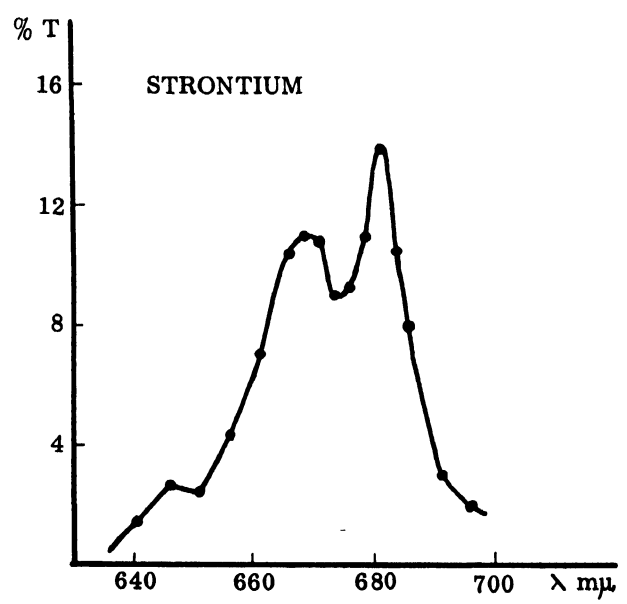

Figure 7

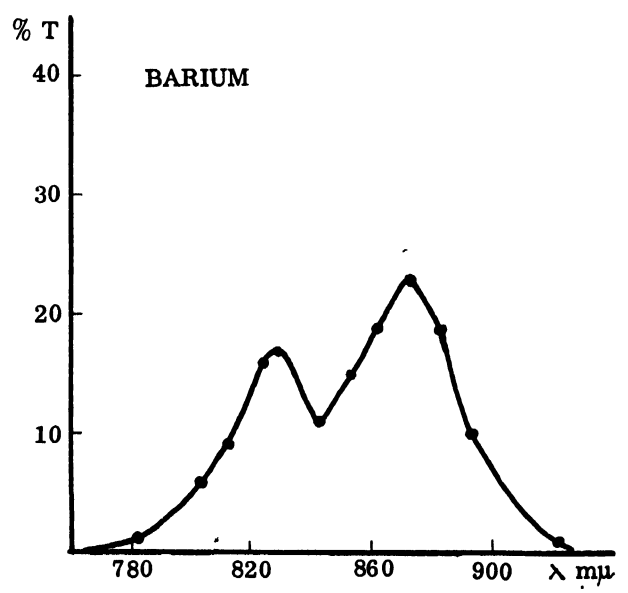

Figure 8

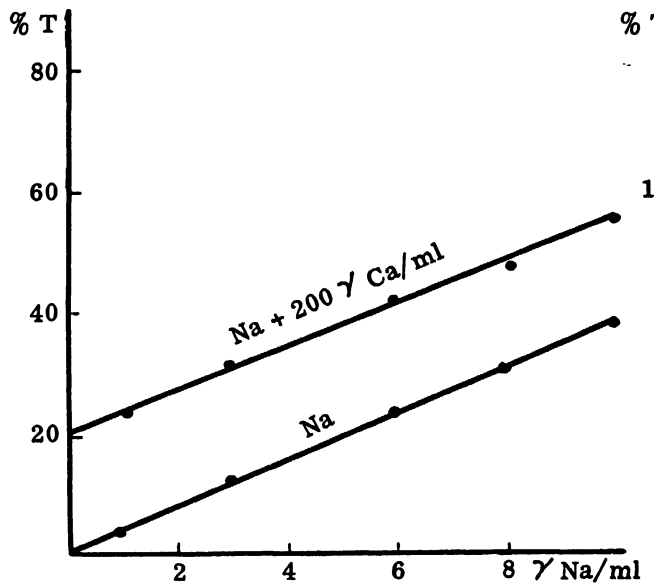

Figure 9

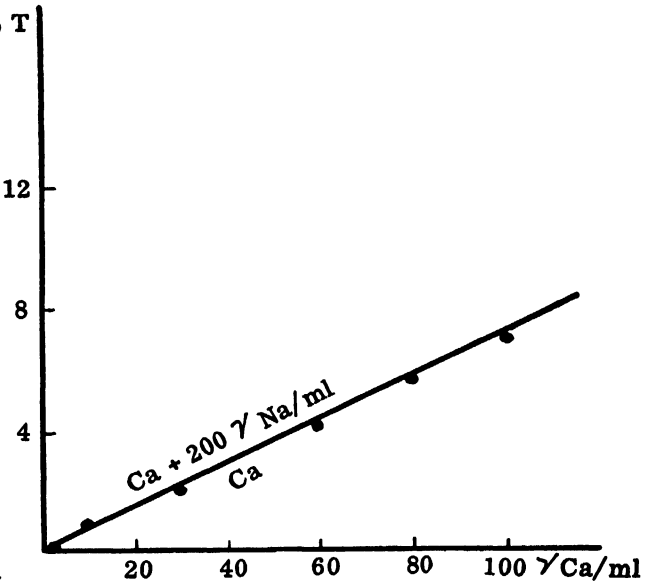

Figure 10

graduated container; small amounts of redistilled water are added until the appropriate volume is made up. This solution contains the alkali metals and alkaline-earth metals.

For the amount of uranium indicated a total separation requires, as a rule, 5 to 7 extractions.

Stringent precautions must be taken to avoid contamination, since the amounts to be determined are minute; this is particularly important in the case of sodium.

The amount of the sample used, the final volume of the aqueous solution after extraction, etc., have been computed, taking into account the maximum tolerances and the sensitivity of the instruments. If changes occur in the latter (for example due to using a photomultiplier) or in the detection limits, the conditions will have to be modified accordingly.

Preparation of standard solutions. Prepared as indicated in Table IV.

Table IV. Standard Solutions

Element	*Concentration (γ/ml)*	*Volume of std. solution to be taken (ml)*	*Final volume (ml)*
Li	10	0.25	25
Na	100	2.50	25
K	100	2.50	25
Rb	100	2.50	25
Cs	100	2.50	25
Ca	100	2.50	25
Sr	200	5.00	25
Ba	500	12.50	25

Reading the Instrument

Conditions are as follows: Wavelength and slit width for each element (see below). Selector valve at 0.1. Gas pressure for the burner: 13 psi for oxygen and 3 psi for acetylene (under these conditions, the flame is wide and of low intensity). Selector key of load resistor at 2 (10,000 megohms).

Read and record the luminosity values (percentage on transmission scale) for the samples and for the standard solutions at the wavelengths and slit widths indicated below.[10]

Sample

λ : 554 mμ; slit : 0.33 mm (M_{Ca})
λ : 589 mμ; slit : 0.10 mm (M_{Na})
λ : 671 mμ; slit : 0.18 mm (M_{Li})
λ : 681 mμ; slit : 0.17 mm (M_{Sr})
λ : 768 mμ; slit : 0.05 mm (M_{K})
λ : 780 mμ; slit : 0.10 mm (M_{Rb})
λ : 852 mμ; slit : 0.20 mm (M_{Cs})
λ : 873 mμ; slit : 0.20 mm (M_{Ba})

Standard Solutions

Calcium
λ : 554 mμ; slit : 0.33 mm (SCa_{Ca})
λ : 589 mμ; slit : 0.10 mm (SCa_{Na})

Sodium
λ : 589 mμ; slit : 0.10 mm (SNa_{Na})

Lithium
λ : 671 mμ; slit : 0.18 mm (SLi_{Li})

Strontium
λ : 681 mμ; slit : 0.17 mm (SSr_{Sr})

Potassium
λ : 768 mμ; slit : 0.05 mm (SK_{K})
λ : 780 mμ; slit : 0.10 mm (SK_{Rb})

Rubidium
λ : 780 mμ; slit : 0.10 mm (SRb_{Rb})
λ : 768 mμ; slit : 0.05 mm (SRb_{K})

Cesium
λ : 852 mμ; slit : 0.20 mm (SCs_{Cs})
λ : 873 mμ; slit : 0.20 mm (SCs_{Ba})

Barium
λ : 873 mμ; slit : 0.20 mm (SBa_{Ba})
λ : 852 mμ; slit : 0.20 mm (SBa_{Cs})

The symbols in parentheses indicate: M, sample; S, standard solutions; SCa, calcium; SNa, sodium, etc.

The subscripts indicate the wavelength of the readings. Thus M_{Ca} is the reading of the sample at the optimal wavelength of Ca, and $S\text{Na}_{Ca}$ is the reading of the sodium-typing solution at the optimal wavelength of calcium.

Subtract from each reading the luminosity value of pure water obtained under similar conditions.

The results are valid only in the cases when none of the elements to be determined is in great excess. Otherwise, the interfering effects would be too strong, and the corrections indicated in the computed formulae would not apply.

It is possible to compute from the dispersion characteristics of the prism, the real band width for each wavelength using the values of the slit width.[9]

Table V. Band Width for Each Wavelength

Element	*Wavelength (mμ)*	*Slit mm*	*Width of band (mμ)*
Ca	554	0.33	10.0
Na	589	0.10	4.6
Li	671	0.18	9.9
Sr	681	0.17	9.5
K	768	0.05	3.2
Rb	780	0.10	6.2
Cs	852	0.20	17.3
Ba	873	0.20	17.8

As a rule, the bands were clearly outlined with the above slit widths; in some cases, however, the low luminous intensity obtained required measurement to be made with wider slits to the detriment of the clarity of the band (Cs and Ba). For sodium and potassium the range can be increased by using wider slits, but, if the sample is rich in these elements the readings may then fall outside the scale. Further dilution would not solve the problem, since it would prevent the detection of some of the other elements.

For this reason, different slits have been chosen, taking the following factors into consideration: (1) the sensitivity required for each element; (2) the response of the instrument; and (3) the use of the same solution for all the readings.

COMPUTATIONS

$$\text{Li } (\gamma/\text{gm U}) = \frac{8.33}{S\text{Li}_{Li}}\left[M_{Li} - \frac{M_{Sr} \times S\text{Sr}_{Li}}{S\text{Sr}_{Sr}}\right]$$

$$\text{Na } (\gamma/\text{gm U}) = \frac{83.3}{S\text{Na}_{Na}}\left[M_{Na} - \frac{M_{Ca} \times S\text{Ca}_{Na}}{S\text{Ca}_{Ca}}\right]$$

$$\text{K } (\gamma/\text{gm U}) = \frac{83.3}{S\text{K}_{K}}\left[M_{K} - \frac{M_{Rb} \times S\text{Rb}_{K}}{S\text{Rb}_{Rb}}\right]$$

$$\text{Rb } (\gamma/\text{gm U}) = \frac{83.3}{S\text{Rb}_{Rb}}\left[M_{Rb} - \frac{M_{K} \times S\text{K}_{Rb}}{S\text{K}_{K}}\right]$$

$$\text{Cs } (\gamma/\text{gm U}) = \frac{83.3}{S\text{Cs}_{Cs}}\left[M_{Cs} - \frac{M_{Ba} \times S\text{Ba}_{Cs}}{S\text{Ba}_{Ba}}\right]$$

$$\text{Ca } (\gamma/\text{gm U}) = \frac{83.3 \times M_{Ca}}{S\text{Ca}_{Ca}}$$

$$\text{Sr } (\gamma/\text{gm U}) = \frac{166.6 \times M_{Sr}}{S\text{Sr}_{Sr}}$$

$$\text{Ba } (\gamma/\text{gm U}) = \frac{417}{S\text{Ba}_{Ba}}\left[M_{Ba} - \frac{S\text{Cs}_{Ba} \times M_{Cs}}{S\text{Ba}_{Cs}}\right]$$

These formulae are sufficiently accurate for analytical needs. Computation by methods of successive approximations would be much more complicated

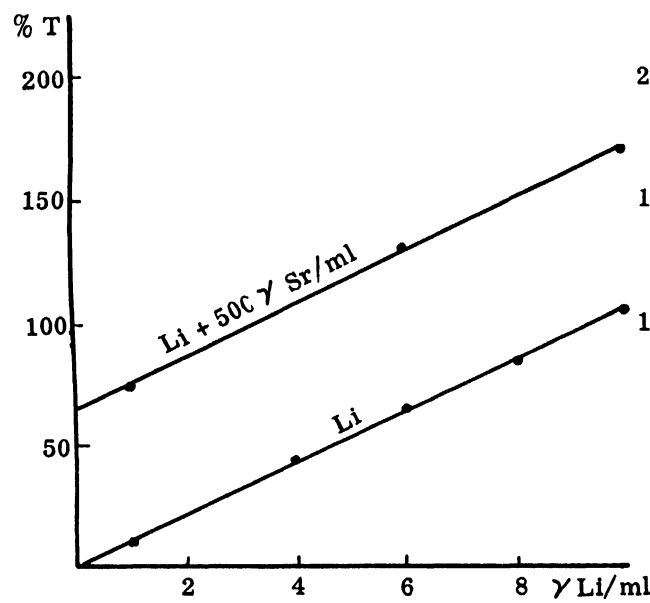

Figure 11

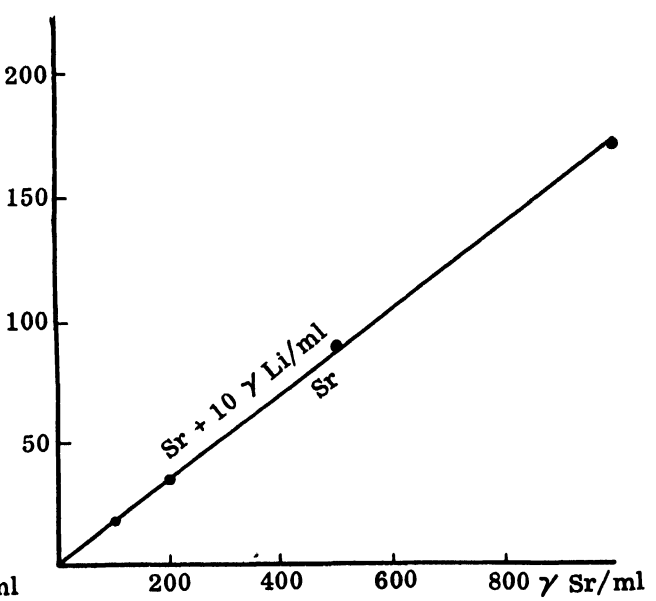

Figure 12

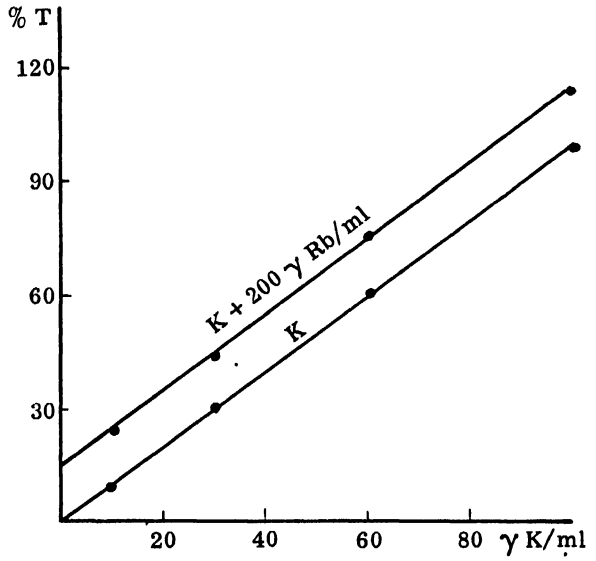

Figure 13

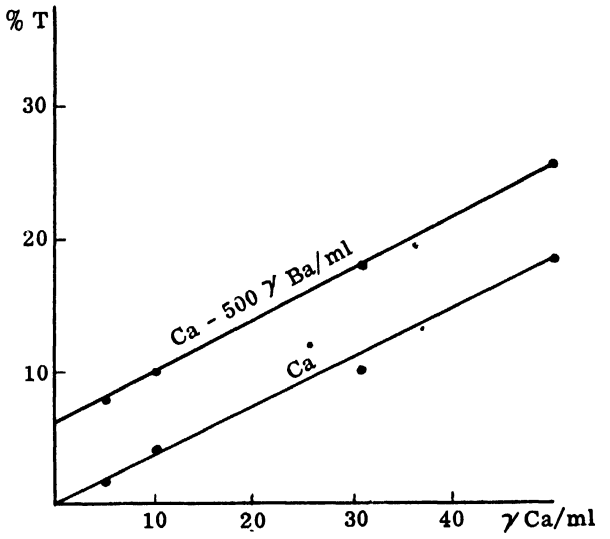

Figure 15

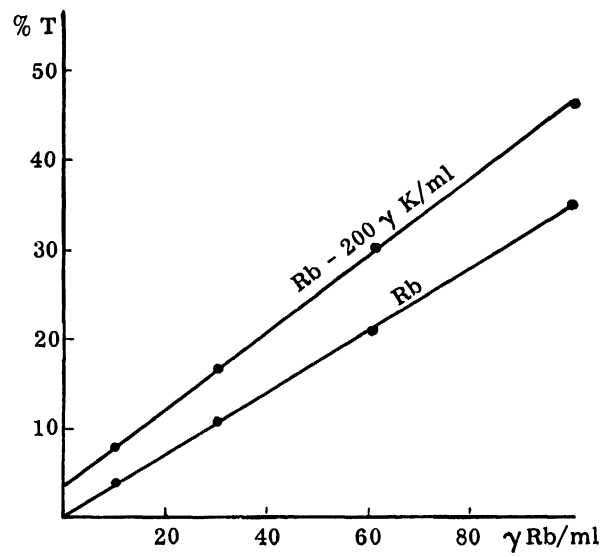

Figure 14

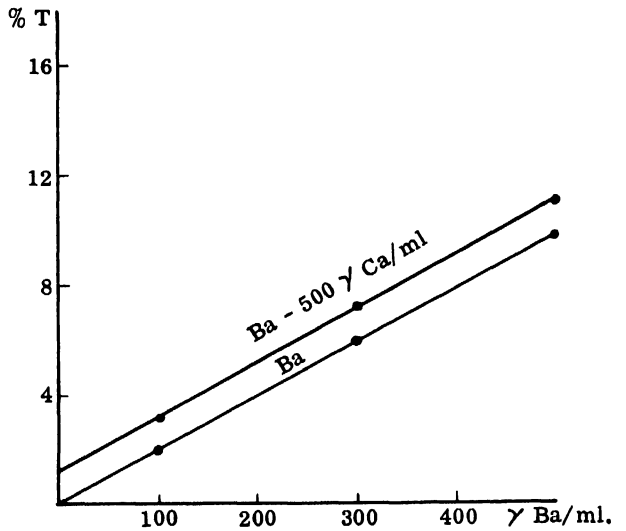

Figure 16

and without much gain in accuracy, since it depends on the precision of the readings in the instrument.

In some cases determinations have been made by comparing the readings of the unknown solution with those of two standard solutions of different concentrations, and comparing the observations with a single standard solution.

The following example shows how the formulae are computed: Let M_{Li} be the reading of the sample at the wavelength of lithium and with the corresponding slit; $S\text{Li}_{Li}$ is the reading of the standard lithium solution under similar conditions; M_{Sr}, the reading obtained with the sample at the wavelength and slits for strontium; and finally $S\text{Sr}_{Sr}$ and $S\text{Sr}_{Li}$ the readings of a standard strontium solution at the wavelengths and with the slit width for strontium and lithium, respectively. The problem is the computation of the lithium content of a sample which also contains strontium. The influence of the strontium is proportional to its concentration, which is:

$$S\text{Sr}_{Sr} \rightarrow 200\ \gamma\ \text{Sr/ml}$$

$$M_{Sr} \rightarrow \frac{M_{Sr} \times 200}{S\text{Sr}_{Sr}}\ \gamma\ \text{Sr/ml}$$

And under the reading conditions for lithium:

$$200\ \gamma\ \text{Sr/ml} \rightarrow S\text{Sr}_{Li}$$

$$\frac{M_{Sr} \times 200}{S\text{Sr}_{Sr}}\ \gamma\ \text{Sr/ml} \rightarrow \frac{M_{Sr} \times 200 \times S\text{Sr}_{Li}}{S\text{Sr}_{Sr} \times 200}$$

Subtracting this latter value from the M_{Li} reading we obtain:

$$M_{Li} - \frac{M_{Sr} \times S\text{Sr}_{Li}}{S\text{Sr}_{Sr}}$$

which is the corrected reading for lithium. To compare with the standard lithium solution (which contains 10 γ/ml):

Table VI

Element	Concentration γ/ml	mμ	Values obtained with Plain phototube* Slit (mm)	%T	Photomultiplier Slit (mm)	%T
Calcium	100	554	0.33	5.8	0.01	15†
Sodium	100	589	0.10	30.7	0.10	75‡
Lithium	10	671	0.18	7.6	0.05	98
Strontium	100	681	0.17	0.9	0.05	7.4

* Phototube No. 2342-1 was used for the blue region and No. 157 for the red (above 625 mμ).
† Photomultiplier in point 3 (sensitivity increases about 15 fold upon passing to "full").
‡ Photomultiplier in point 2 (sensitivity increases about 17 fold upon passing to "full").

$$S\mathrm{Li}_{\mathrm{Li}} \rightarrow 10 \text{ Li/ml}$$

$$M_{\mathrm{Li}} - \frac{M_{\mathrm{Sr}} \times S\mathrm{Sr}_{\mathrm{Li}}}{S\mathrm{Sr}_{\mathrm{Sr}}} \rightarrow \frac{10}{S\mathrm{Li}_{\mathrm{Li}}}$$

$$\left[M_{\mathrm{Li}} \frac{M_{\mathrm{Sr}} \times S\mathrm{Sr}_{\mathrm{Li}}}{S\mathrm{Sr}_{\mathrm{Sr}}}\right] \quad \gamma \text{ Li/ml}$$

And since the reading was taken in 5 ml of the solution obtained from the extraction of 6 gm uranium, multiply the above by 5/6 giving:

$$\mathrm{Li}\ (\gamma/\mathrm{gmU}) = \frac{8.33}{S\mathrm{Li}_{\mathrm{Li}}} \left[M_{\mathrm{Li}} - \frac{M_{\mathrm{Sr}} \times S\mathrm{Sr}_{\mathrm{Li}}}{S\mathrm{Sr}_{\mathrm{Sr}}}\right]$$

CONCLUSIONS

The application of flame spectrophotometry to the evaluation of the alkali metal and alkaline earth metal contents in uranium and its compounds was studied.

1. The spectra of the alkali metals and alkaline earths were obtained.

2. Calibration curves for all these elements were plotted, and a study was also made of the mutual influences of those elements emitting at wavelengths close to each other.

3. The most convenient method for the separation of the uranium was chosen, and the most favorable conditions for ether extraction were determined.

4. It has been proved that, with the proposed method, recovery of elements studied is quantitative.

5. The methods of measurement with the instrument used are described, and a computation method is offered.

Tables with the experimental data obtained are included in each case.

Note: A subsequent paper (Julia F. Possidoni de Albinati: "Valoración de lantano, hierro y magnesio por espectrofotometría de llama"; presented at the 6th Latin American Convention on Chemistry, Caracas, May 1955) has demonstrated that the use of the photomultiplier (1P28) produces much higher sensitivities in the determination of calcium, sodium, lithium and strontium. Table VI gives some numerical examples.

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Estimation of Traces of Gallium, Indium and Thallium by Flame Spectrophotometry, its Application in the Analysis of High Purity Uranium

By A. E. Lagos,* Argentina

Subgroup IIIB of the periodic system consists of the elements gallium, indium and thallium, which are of very rare occurrence and, until now, of no great industrial significance. They form + 3 oxidation compounds and, in the case of thallium, + 1. The + 3 compounds are similar to those of aluminum. The acidity of the hydroxides decreases with atomic weight, while the oxidation potential of the ions increases with it.

These elements readily give up their first electron, so that their compounds produce characteristic colors in flames.

FLAME SPECTROPHOTOMETRY

One of the earliest spectroscopic techniques was that whereby spectral lines were obtained by exciting hot vapors introduced into a flame.

Real flame spectrophotometry began with the work of Lundergardh.[1] Although the original Lundegardh method was substantially modified with the object of simplifying instrumentation, the principle is the same and consists of the continuous injection of the solution to be analyzed into an oxyacetylene or oxhydrogen flame, thus into a source having a large heating capacity. The atoms of the elements contained in the solution are excited, emitting radiation of characteristic wavelengths, the luminous intensity of which is measured photometrically after suitable isolation, by means of a prism, diffraction grating or filter, of the wavelength considered as optimal, for the elements to be determined. At present, the light intensity of the spectral line considered is measured using phototubes. For some of these elements, the sensitivities have been determined with a Beckman spectrophotometer,[2] while, for the elements Cd, Gd, Ga, Au, In, Hg, Gd, Rh, Ru, Ag, Sr and Tl, the Lundegardh values are given as established by flame spectrography.

Table I shows the maximum tolerances set for gallium, indium and thallium respectively, considered as impurities in the uranium.

This paper deals with the study of a method for the evaluation of gallium, indium and thallium present in high purity uranium.

Flame spectrophotometry must meet the following analytical requirements:

(*a*) Adequate sensitivity: The lower limits for the amount evaluated should be a few γ for the three elements (Table I).

(*b*) Specificity: Inasmuch as it is necessary to avoid interference from other radiation, work on each element should be undertaken at the optimum wavelength and minimum slit width compatible with the sensitivity.

(*c*) Linearity of the relationship between the concentration of the elements and the luminous intensity of the radiation within the concentration range required is needed.

Reagents

(*a*) Standard gallium, indium and thallium solutions, as nitrates, having a nitric acid acidity of 3% are prepared with spectroscopically pure chemicals. The 1 mg/ml concentration of these solutions is determined gravimetrically. Dilute solutions are prepared as and when needed, from the standard solutions previously prepared.

(*b*) Uranyl nitrate free from gallium, indium and thallium.

(*c*) Nitric acid, pure, redistilled.

(*d*) Ethyl ether, free from peroxide and alcohol.

(*e*) Water: redistilled in quartz apparatus.

Equipment and Instruments

(*a*) Flame spectrophotometer: the Beckman D.U. flame spectrophotometer is used with flame attachment (No. 9200); oxyacetylene atomizer burner (4030); special phototubes for flames (No. 157); photomultiplier (1P28).

(*b*) Oxygen and acetylene from cylinders of commercially available types.

(*c*) Quartz still, for redistillation.

(*d*) Quartz decanting flasks.

(*e*) Volumetric material: calibrated pipettes, 5–2 and 1 ml; calibrated beakers, 25 ml; calibrated test tubes, 3 ml.

(*f*) Quartz precipitation vessels, 30 ml.

Original language: Spanish.

* Comisión Nacional de la Energía Atómica.

DESCRIPTION OF METHOD

Separation of Uranium

In order to avoid contamination by the dispersion products of the spectrophotometer burner from solutions which may contain such a toxic and radioactive substance as uranium, it is necessary to separate the latter from gallium, indium and thallium, and to burn only a solution of these elements. The separation should be made from uranyl nitrate. If the sample is metallic uranium, UO_3 or U_3O_8, it should be dissolved in nitric acid and heated until it is just dry. The amount to be treated is 5 gm of uranium or its equivalent in uranyl nitrate, UO_3, U_3O_8 etc.

Separation of the uranium is undertaken by extraction with ether,[3,4,5] making sure that quantitative amounts of gallium, indium and thallium remain on the aqueous layer. The most convenient method is afforded by ether extraction from an aqueous acid phase of 4 to 5*M* nitric acid, the extraction coefficient under these conditions being 2.3. The separation is made as follows: uranium nitrate crystals are transferred to a quartz decanting flask, 3 ml of redistilled water are added along with 2 ml HNO_3 and 20 ml of ether (alcohol and peroxide free). Stir for one minute, decant and separate the ether layer. Repeat the extraction with 20-ml ether fractions, adding 2 ml of nitric acid before each of them in order to replace the acid dissolved in the ether used for the previous extraction. Not more than 5 extractions are needed for 5 gm quantities of uranium, but these are repeated until the ether extraction is colorless.

The aqueous layer, free from uranium, and the washing residues obtained with redistilled water, are transferred to a 30-ml quartz vessel, after which the liquid is evaporated down to 1 ml, and made up to 3 ml in a calibrated tube.

This is the solution used to take the readings.

Spectophotometric Readings

The reading conditions are as follows:[6,7] (*a*) wavelengths (Table II) and slit widths suitable for each element; (*b*) gas pressures for the burner: oxygen, 15 psi, acetylene 3 psi, giving a flame of low brightness; (*c*) selector knob of the load resistance at 2 (22 megohms); (*d*) photomultiplier at maximum sensitivity; (*e*) sensitivity at maximum (counterclockwise stop).

Readings are always made immediately after zero adjustment of the reference current ("dark current") and against a redistilled water bank.

EXPERIMENTAL PART

Spectophotometry of Gallium, Indium and Thallium

Gallium, Indium and Thallium Flame Spectra

To obtain the spectra of these three elements, three standard solutions of each were used, and light intensities were represented in *T*%, as a function of γ.

In each case, the concentration of the solution was 1 mg of each element per ml, and the reading conditions used in all cases were for maximum sensitivity: slit width, 0.05 mm; selector knob at position 1; O_2 pressure, 15 psi; C_2H_2 pressure, 3 psi.

Table I

Element	*Maximum tolerance, gm/gm*
Gallium	10^{-6}
Indium	10^{-6}
Thallium	10^{-6}

Table II

Element	*Optimum λ in mμ*
Gallium	417.2
Indium	451.1
Thallium	377.5

Figures 1, 2 and 3 show the results obtained for gallium, indium and thallium, respectively.

The spectral shapes allow the use of very narrow bands, which is of advantage in avoiding the influence of flame fluctuations due to the high sensitivity of the device. Furthermore, the shape and position of the peaks make it possible to predict the non-interference of one element in the determination of the others.

The low intensity of the radiation emitted by the elements gallium, indium and thallium, as compared to those which correspond to the alkali and alkaline earth elements justifies a forecast of interference on the part of the later while making determinations pertaining to the former. It will also be necessary to look into possible interference by other elements which emit at wavelengths close to the optimum wavelengths of gallium, indium and thallium.

It will be noted from Figs. 1, 2 and 3, that gallium shows a main peak at 417.2 mμ, and a secondary peak at 403.3 mμ. Indium shows its main peak at 451.1

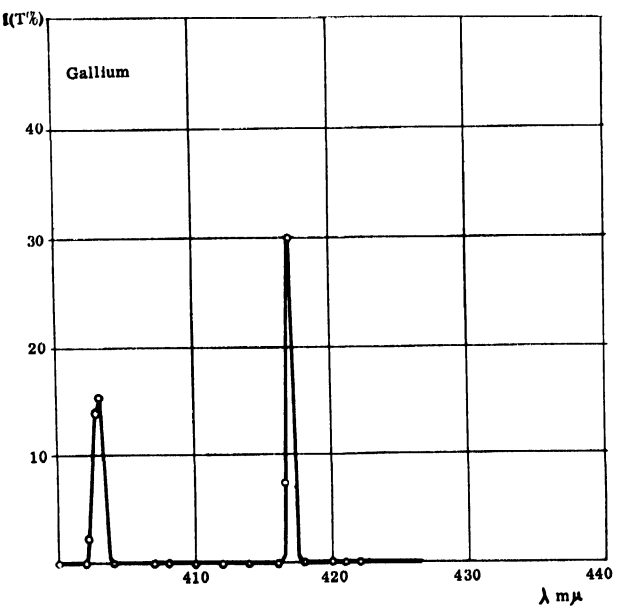

Figure 1

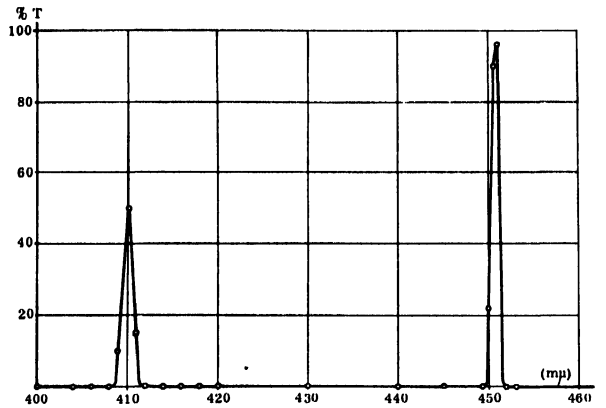

Figure 2. Indium

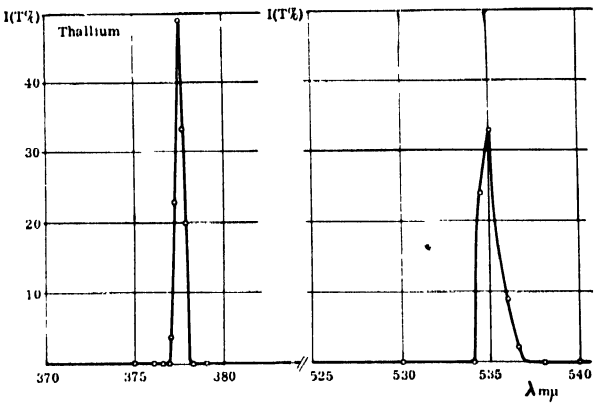

Figure 3. Thallium

mμ, with a secondary peak at 410.1 mμ, and thallium produces a main peak at 377.5 mμ, with a secondary peak at 535 mμ.

Table II gives the optimum wavelengths for gallium, indium and thallium.

Calibration Curves

An attempt was made to verify the linearity of concentrations in the solutions to be analyzed and the luminous intensities obtained, within a certain margin. The conditions under which the readings were taken were established experimentally for each element in order to obtain a high sensitivity, compatible with the high precision of the data obtained.

The calibration curves of the elements under study (Figs. 4, 5 and 6) were obtained working at the optimum wavelengths for each case (Table II). The reading conditions were those previously used, except for the slit width, which was set at 0.1 mm.

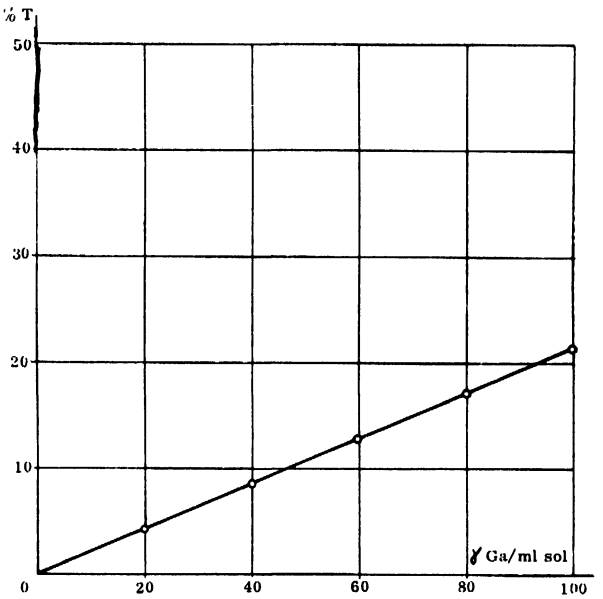

Figure 4

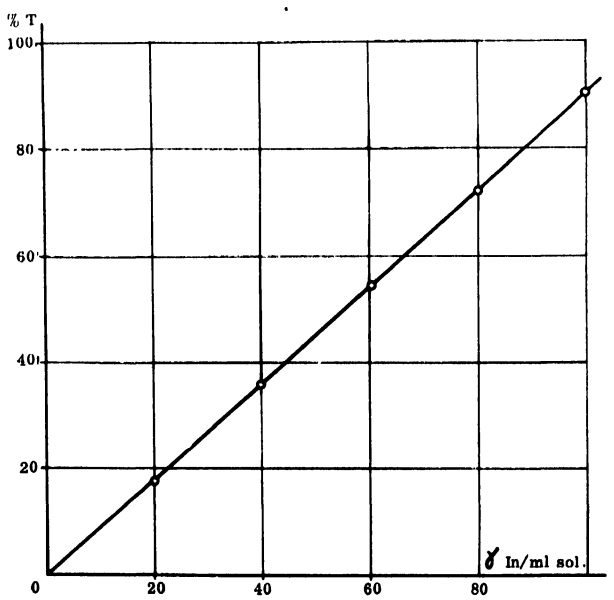

Figure 5

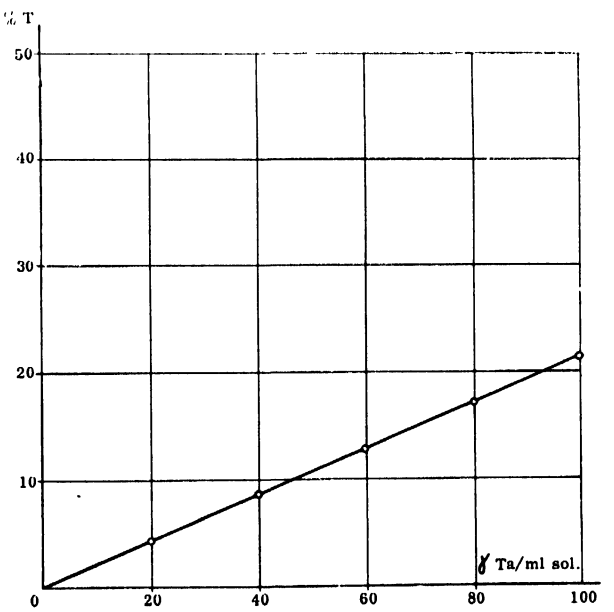

Figure 6

Table III

Element	Lower detection limit (γ/ml)
Gallium	1
Indium	0.2
Thallium	1

Table IV

Element	Actual γ/ml	Obtained γ/ml
Gallium	100	100
Indium	100	100
Thallium	100	100

Table V

Element	Actual γ/ml	Obtained γ/ml		
		417.2 mμ	451.1 mμ	377.5 mμ
Gallium	100	100	0	0
Indium	100	0	100	0
Thallium	100	0	0	100

Figures 4, 5 and 6 show that there is a linear relation between concentration and intensity. Furthermore, the detection limits which arise out of the analysis of these figures can be reduced by a factor 10 by setting the selector knob at 0.1. These conditions produce Table III.

Mutual Interference

A solution was prepared of gallium, indium and thallium containing 100 γ of each per ml of solution and the optimum wavelengths were read for each element, which gave the values shown on Table IV.

We prepared three solutions of gallium, indium and thallium with 100 γ of metal per ml of solution, and read them at their optimum wavelengths, as well as at the optimum wavelengths for other elements, which gave the following values (Table V). This shows that there is no mutual interference between these elements.

Application

The existence of a linear relationship between the intensities and concentrations has been proved; therefore, by reading the luminous intensity of an unknown sample, the luminous intensity for a known standard concentration and that for a redistilled water blank, it is possible, by a simple proportion, to obtain the concentration of the unknown. This method of measurement rules out the errors due to the dark current during a series of reading and also to sensitivity variations of the equipment.

A series of samples were analyzed according to the procedure outlined above, which gave the results shown in Table VI.

Separation of Gallium, Indium and Thallium from Uranium

Uranium nitrate free from gallium, indium and thallium was used. Known quantities of gallium, indium and thallium are added to 5 gm of uranium in the form of uranyl nitrate, and nitric acid to a concentration of 4–5 *M*. Five extractions are made with 20 ml fractions of ether. After each extraction 1 ml nitric acid is added to the aqueous layer, in order to re-establish the acidity. The aqueous phase is then transferred to a quartz crucible, evaporated until almost dry, brought up to 3 ml in a calibrated tube and then used for measurements. The readings obtained with redistilled water are compared with standards of known concentration.

This method of separation was tested giving the values appearing in Table VII.

The results obtained are such as to warrant the claim that the separation of gallium, indium and thallium from uranium by ether extraction is efficient.

Table VI

Element	Sample 1		Sample 2		Sample 3		Sample 4	
	Added γ/ml	Meas. γ/ml	Added γ/ml	Meas. γ/ml	Added γ/ml	Meas. γ/ml	Added γ/ml	Meas. γ/ml
Gallium	100	100	10	10	100	100	100	100
Indium	100	97	100	100	10	10	100	100
Thallium	100	100	100	100	100	100	10	9

Table VII

Element	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	Added γ/ml	Recov. γ/ml	Added γ/ml	Recov. γ/ml	Added γ/ml	Recov. γ/ml	Added γ/ml	Recov. γ/ml	Added γ/ml	Recov. γ/ml
Gallium	100	99	100	100	100	104	100	100	100	101
Indium	100	100	100	97	100	95	50	50	10	10
Thallium	100	97	100	99	100	100	100	95	50	50

Interferences

To check the influence of other elements in the determination of gallium, indium and thallium, the luminous intensities corresponding to a series of elements at the optimum wave lengths of Ga, In and Tl were measured. This series of elements includes, not only those emitting radiations near the wavelengths of Ga, In and Tl, but also almost all those detectable on the Beckman spectrophotometer with the oxyacetylene flame.

Table VIII lists the determinations made with solutions of each element prepared with spectroscopically pure chemicals.

Table IX shows the equivalents in gallium, indium and thallium, of the possible interferences studied.

Table X shows the maximum quantity of each element studied which does not interfere in the spectrophotometry of gallium, indium or thallium, when these are in concentrations of the order of 10^{-4}, 10^{-5} and 10^{-3}, respectively. When smaller amounts are to be evaluated, the indicated tolerances should be proportionally smaller.

The activity of Ga, In or Tl, as well as that of each of the interfering elements, has been checked by the use of artificially prepared mixtures. For the cases in which these are found in concentrations greater than those tolerated in the photometry of Ga, In and Tl (Table X), the luminous intensity values obtained at the optimum wavelengths of each are corrected, eliminating those producing interferences at those same wavelengths.[8]

Table VIII

Element	*Sol. used* γ/ml,	*T% at* 377.5 mμ	*T% at* 417.1 mμ	*T% at* 451.1 mμ
Tl	100	31.5	0	0
Ga	100	0	24	0
In	10	0	0	9
Li	50	0	0	0
Na	100	1	1	1.0
K	100	1	1.1	1.3
Rb	1000	0	3.1	4.5
Cs	50	0	0	0
Mg	1000	28.5	2.0	2.4
Ca	1000	10.0	6.5	9
Sr	100	0	0.7	0.4
Ba	1000	0	2.8	7.2
La	1000	0	2.0	4.5
Fe	100	0.9	0.3	2.1
Cd	10	0	0	0
Cr	100	0	0	0
Co	10	0	0	0
Mo	100	0	0.2	0.2
Ni	100	0	0	0
Mn	10	0	0	0
B	10	0	0	0
Cu	100	0	0	0
Ag	10	0	0	0
Ti	100	0.2	0.2	0.5
V	100	0	0	0
Al	1000	0	0	0
Sb	100	0	0	0
Zn	100	0	0	0
Pb	10000	0.2	0	0.5
Hg	10	0	0	0
Pt	100	0	0	0
Pd	100	0	0	0
Bi	100	0	0	0.2
Nd	100	0	0	0
Zr	100	0	0	0

Table IX

Element	*Sol. used,* γ/ml	*At* 377.5 mμ *x* γ *of element is equiv. to* γ *Tl*	*At* 417.1 mμ *x* γ *of element is equiv. to* γ *Ga*	*At* 451.1 mμ *x* γ *of element is equiv. to* γ *In*
Tl	1000	1000	0	0
Ga	100	0	100	0
In	10	0	0	10
Li	50	0	0	0
Na	100	3.1	25	15.4
K	100	3.1	27	16.3
Rb	1000	0	14.5	8.2
Cs	50	0	0	0
Mg	1000	90.4	0	0
Ca	1000	31.7	104.1	82
Sr	100	0	0	0
Ba	1000	0	125	0
La	1000	0	0	0
Fe	100	3.1	8.3	1.8
Cd	10	0	0	0
Cr	100	0	0	0
Co	10	0	0	0
Mo	100	0	4.1	4.5
Ni	100	0	0	0
Mn	10	0	0	0
B	10	0	0	0
Cu	100	0	0	0
Ag	10	0	0	0
Ti	100	0	1	0.5
V	100	0	0	0
Al	1000	0	0	0
Sb	100	0	0	0
Zn	100	0	0	0
Pb	10000	0	0	0.5
Hg	10	0	0	0
Bi	100	0	0	0
Pt	100	0	0	0
Pd	100	0	0	0
Nd	100	0	0	0
Zr	100	0	0	0

Table X

Element	*γ/ml permitting Tl photometry*	*γ/ml permitting Ga photometry*	*γ/ml permitting In photometry*
Li	50	50	50
Na	100	100	50
K	100	100	33
Rb	1000	300	100
Cs	50	50	50
Mg	500	500	200
Ca	750	200	50
Sr	100	100	100
Ba	1000	500	50
La	1000	500	100
Fe	100	100	20
Cd	10	10	10
Cr	100	100	100
Co	10	10	10
Mo	100	100	100
Ni	100	100	100
Mn	10	10	10
B	10	10	10
Cu	100	100	100
Ag	10	10	10
Ti	100	100	100
V	100	100	100
Al	1000	1000	1000
Sb	100	100	100
Zn	100	100	100
Pb	10000	10000	10000
Hg	10	10	10
Pt	100	100	100
Pd	100	100	100
Bi	100	100	100
Nd	100	100	100
Zr	100	100	100

SUMMARY

A method is proposed for the evaluation of gallium, indium and thallium by flame spectrophotometry, and its application to the estimation of these elements in uranium and its compounds.

(*a*) The spectra of gallium, indium and thallium were obtained.

(*b*) Calibration curves for these same elements were drawn.

(*c*) The separation of gallium, indium and thallium from uranium by ether extraction from the nitrates in a nitric acid medium was studied, and it was shown that it is quantitative under the conditions established.

(*d*) Interferences are studied, and a method for correcting them is suggested.

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Estimation of Lanthanum, Iron, and Magnesium by Flame Spectrophotometry

By Julia Flavia Possidoni de Albinati,* Argentina

The use of flame spectrophotometry for the evaluation of lanthanum, iron and magnesium in uranium and its compounds has been studied.

Flame emission of these elements can be used for analysis employing oxyacetylene or hydrogen-oxygen burners.[1,2]

After the extraction of uranium with ether the nitric acid medium of about 4*M* contains the following elements in the aqueous phase: alkali metals, alkaline earth metals,[3] gallium, indium, thallium,[4] iron, magnesium, and lanthanum.

A study has been made of the possibility of determining iron, magnesium, and lanthanum together or by the separation of the iron as a chloride in 6*M* hydrochloric medium.

REAGENTS AND APPARATUS

1. Nitric acid: distilled in quartz and kept in a quartz or "Vycor" container.
2. Hydrochloric acid: same as above.
3. Redistilled water: in quartz.
4. Ethyl ether: Freed from peroxides and alcohol by distillation from ferrous sulfate and washing with redistilled water.
5. Standard solutions of magnesium, iron, and lanthanum: prepared with spectroscopically pure chemicals and redistilled water. Concentrations (ca 1 mg/ml) were established gravimetrically. Kept in polyethylene containers. Diluted solutions were prepared immediately before use. The same precautions were observed for the other elements under study.
6. Quartz still: A Heraeus still was used.
7. Flame spectrophotometer: Beckman model DU with flame attachment (No. 9200), oxyacetylene burner (No. 4030), hydrogen-oxygen burner (No. 4031), phototube for the red zone (No. 157) and photomultiplier (IP38) for the blue and the ultraviolet.
8. Decanting ampules: with additional attachment permitting separation of the ether phase.
9. Volumetric flasks: controlled pipettes, burettes, and beakers.
10. Glassware and capsules: quartz.

EMISSION SPECTRA OF IRON, LANTHANUM AND MAGNESIUM

Emission spectra were obtained with the oxyacetylene burner and, for magnesium, with the hydrogen-oxygen burner as well.

The lanthanum spectrum displays three clearly defined maxima (Fig. 1) of which the 565 nμ peak is the most sensitive; however, since in this line there is considerable interference from other elements, the 440 mμ peak is more convenient for estimation. It was obtained with 1 mg/ml of lanthanum solution.

The iron spectrum is quite complex and presents four peaks between 358 and 393 mμ; among these, the 372 mμ is the most convenient for analytical purposes. It also displays intense luminosity over a broad region of the spectrum. It was obtained with 250 γ/ml iron solution (Fig. 2).

Two peaks were observed in the magnesium spectrum (Fig. 3) and both are convenient for evaluation (371 and 383 mμ), but only one of them is sensitive in the hydrogen-oxygen burner (Fig. 4) at 285 mμ. This was obtained working with 1 mg/ml magnesium solution.

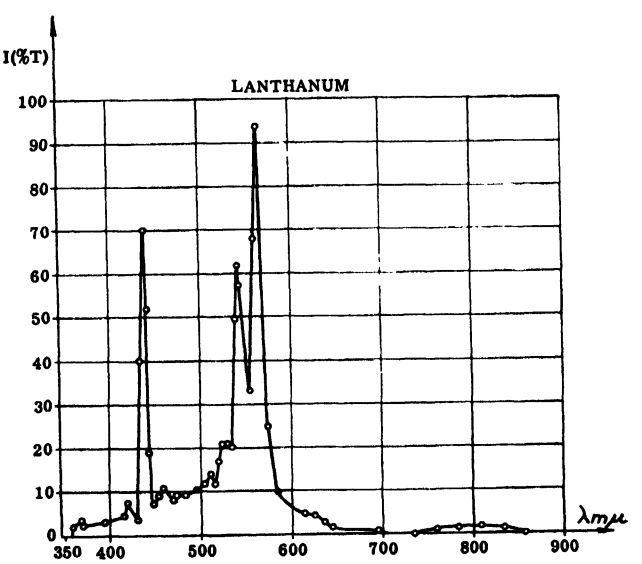

Figure 1

Original language: Spanish.

* Comisión Nacional de la Energía Atómica.

Table I. Effect of Acetylene Pressure Change. Oxyacetylene Burner, Oxygen Pressure: 10 psi

Pressure of C_2H_2, psi	*Intensity, % T*
2.5	7.–
3.0	13.–
3.5	17.–
4.0	22.5
4.5	26.-
5.0	30.–
5.5	33.–
6.0	35.–
6.5	38.–

Table II. Effect of Oxygen Pressure Change. Oxyacetylene Burner, Acetylene Pressure: 3 psi

O_2 pressure, psi	*Intensity, % T*
5.0	15.–
6.0	16.8
7.0	16.5
8.0	15.0
9.0	13.5
10.0	12.5
12.0	8.7
14.0	7.0
15.0	6.0

WORKING CONDITIONS FOR APPARATUS

Influence of Pressures of Burning Gas

It has been shown that it is important to adjust exactly the gauge pressures of the gases feeding both types of burners; these values are given in Tables I, II, and III. In each case, a 1000 γ/ml magnesium solution was used and was read against redistilled water.

It was observed that an increase in gas pressure increased the intensity of radiation (besides increasing the luminosity of the flame). This is due to the rise in temperature of the source and, also to the higher consumption rate of the solution.

On the other hand, an increase in oxygen pressure causes the radiation intensity to decrease (after each optimal value) because of the cooling of the exciting source.

Sensitivity

The influence of the sensitivity of the instrument on the results, was established.

Figure 5 was obtained using a lithium solution (10 γ/ml), other conditions being the same. Each reading was taken against redistilled water, adjusting the galvanometer to zero with the dark-current dial.

The convenience of working with the sensitivity dial at the counterclockwise limit when the reading requires maximum sensitivity[5,6] is apparent from Fig. 5.

However, when the dark current is not absolutely steady, it is advisable to move the dial to positions closer to the clockwise limit.

Slits

In each case, the slits were selected so as to make it possible to obtain the maximum sensitivity compatible with the greatest resolution, reducing interference and the background effects to a minimum. We preferred to increase the sensitivity with the selector dial at 0.1 and the sensitivity dial at the counterclockwise limit.

Limits in the Use of Photomultipliers

The limit of use of this attachment[7] was established in order to determine at which wavelengths it may be used conveniently in conjunction with a phototube for the red region (starting at 625 mμ).

Work was done on solutions of different metals

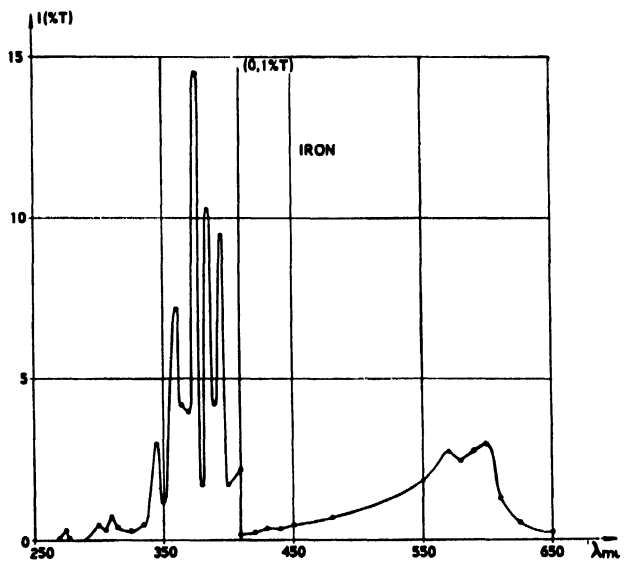

Figure 2

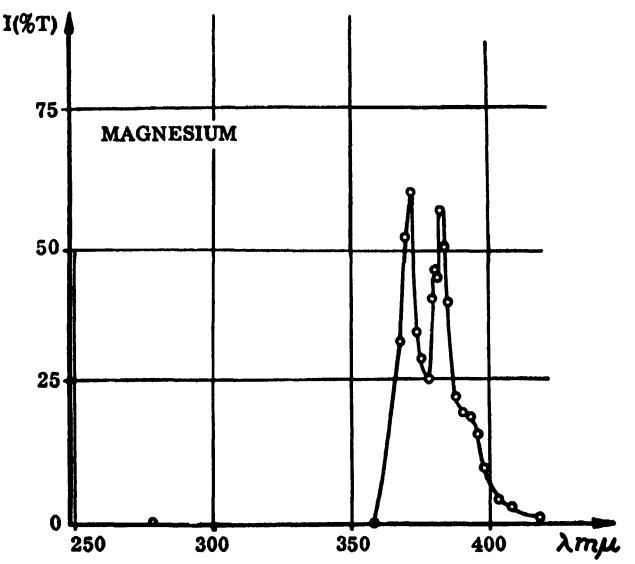

Figure 3

Table III. Effect of Hydrogen Pressure Change. Hydrogen-Oxygen Burner, Oxygen Pressure: 15 psi

H_2 pressure, psi	Intensity, % T
3.0	0
4.0	1.3
5.0	4.7
6.0	8.5
7.0	12.8
8.0	17.5
9.0	20.2

to make possible a study of the spectral region in which phototube No. 157 could be used.

Table IV shows that the photomultiplier may be used to advantage up to 700 mμ.

Influence of the Position of the Selector Dial of the Photomultiplier

Table V shows that it is advisable to work with the dial at "full" to investigate the traces of the elements, and at the same time the advantage of the other positions for higher concentrations which cause instability of the galvanometer needle and even prevent the readings altogether since they fall outside the scale. A 100 γ/ml calcium solution was used.

SELECTION OF BURNER FOR EVALUATION OF MAGNESIUM

The data obtained with both appliances were compared. Table VI shows that while the 285 mμ line is more clearly outlined with the hydrogen-oxygen burner, the sensitivity at 372 and 383 mμ is only about 10% of that obtained with oxyacetylene.[8]

SELECTION OF BEST WAVELENGTH FOR LANTHANUM EVALUATION

It was mentioned earlier that the 440 mμ line is more convenient than the more sensitive 565 mμ line since it suffers less from the interference of other elements, particularly calcium, which makes the lanthanum readings at 565 mμ impossible (Table VII).

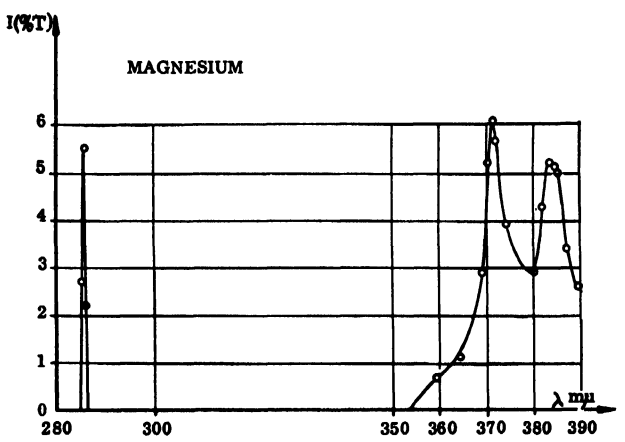

Figure 4

CALIBRATION CURVES

The calibration curves for the three elements under study, conformed to the linear law within the concentration ranges of interest. These curves can not be taken as standard, since even small differences in the working conditions of the instruments lead to different values. Therefore, the readings of the sample and standard solutions should be made jointly, adjusting the galvanometer to zero with redistilled water, using the dark current dial. It is indicated that the concentration of the sample and standard solutions should be of the same order of magnitude (Figs. 6, 7 and 8).

INTERFERENCES IN THE EVALUATION OF LANTHANUM, IRON AND MAGNESIUM

We determined the mutual interference between lanthanum, iron, and magnesium on the one hand, and the alkali metals, alkaline earths, gallium, indium, and thallium, on the other.

These observations are recorded in Tables VIII and IX.

The selector dial of the photomultiplier was at "full" and load resistance of 2 (22 megohms) was used up to 700 mμ.

Table IV. Limits of Use of Photomultiplier

Element	Concentr., γ/ml	Wavelength, mμ	Phototube no. 157		Photomultiplier	
			Slit	% T	Slit	% T
Lithium	10	671	0.18	7.6	0.05	98.–
Strontium	100	681	0.17	0.9	0.05	7.4
Potassium	100	768	0.05	7.3	0.05	2.4
Cesium	100	852	0.20	10.6	0.20	1.3
Barium	500	873	0.40	1.8	0.40	0

Table V. Influence of the Position of Selector Dial

Selector dial position	Reading, %T
1	0.3
2	1.5
3	7.–
4	28.–
Full	105.–

Table VI. Influence of the Burner in the Case of Magnesium Evaluation

Burner	Oxygen pressure, psi	Acetylene pressure, psi	Hydrogen pressure, psi	Slit, mm	λ mμ	Luminous intensity, % T
Oxyacety-	10	3	—	0.10	285	0.5
lene	10	3	—	0.10	372	60.–
	10	3	—	0.10	383	57.–
Oxygen-	15	—	5	0.10	285	5.6
hydrogen	15	—	5	0.10	372	6.1
	15	—	5	0.10	383	5.2

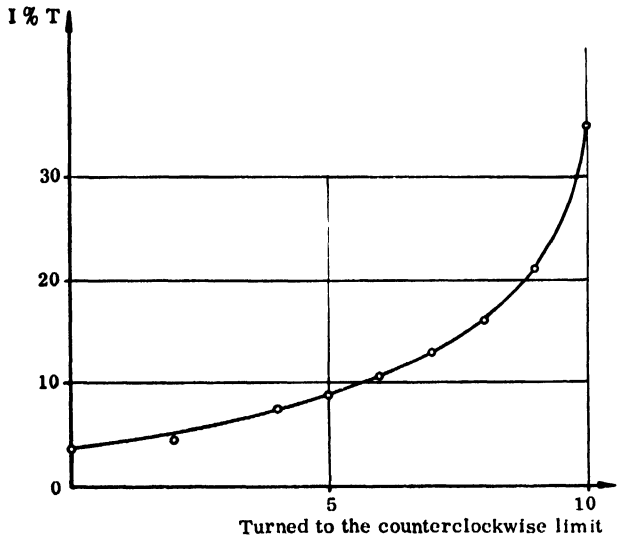

Figure 5

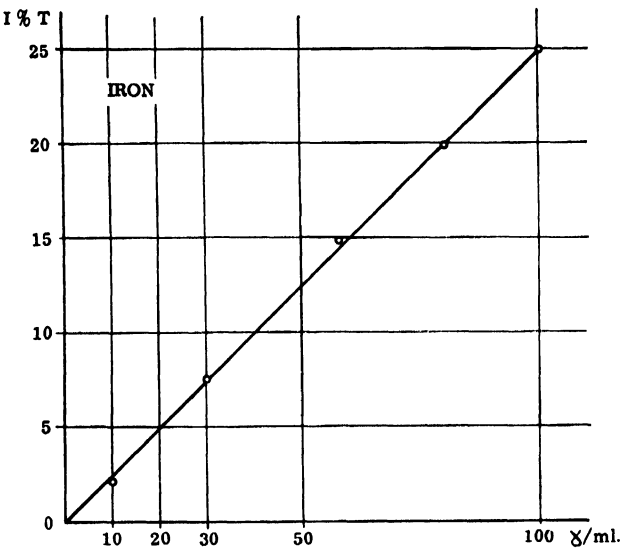

Figure 7

As a result, all the elements except iron can be measured easily, making the necessary corrections for the other elements the sample may contain.[3]

This applies to the values of the concentrations indicated. Moreover, large amounts of an element that does not emit radiation at the optimum wavelength of another, may affect the readings of the latter.[9] Strange mentions that magnesium and aluminium lower the intensity of Li, and Servigne and Guerin[10] have proved that Al affects calcium. We have observed that Al lowers the luminous intensity of magnesium.

Iron cannot be measured in the presence of magnesium; calcium, lanthanum, and rubidium are also interfering elements. In this case its separation is convenient, extraction being made with ether in 6*M* hydrochloric acid medium.

INFLUENCE OF CERTAIN ACIDS

Since the readings obtained are not independent of the acids present in the solution in which the lanthanum, iron, and magnesium are studied, it is necessary to determine the nature and amount of the acid.[11]

Table X includes some of the values obtained during the investigation of this matter.

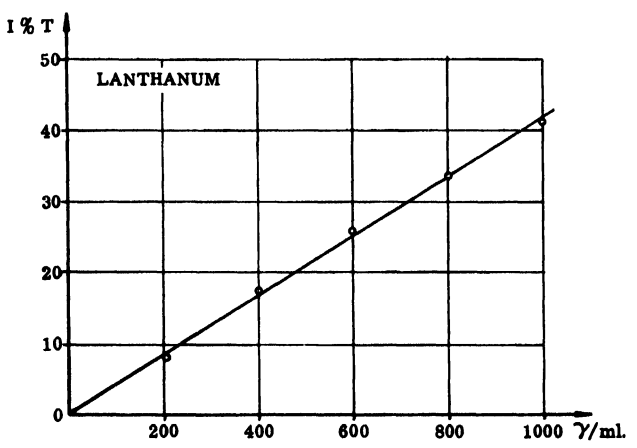

Figure 6

PROCESS USED

Separation of Uranium

The sample (about 10 gm uranium content) is converted to the nitrate and then evaporated almost to dryness. The crystals are transferred to a separation funnel and the uranium is extracted with ether in a nitric acid medium of about 4*M* (2.5 nitric acid in 10 ml of solution). For this purpose, 20–25 ml ether fractions are added; also, in order to maintain acidity, 2 ml nitric acid are added before each extraction. Extractions are repeated until the ether and aqueous phases are absolutely colorless. If iron is present, it will color the aqueous phase in this case, however, the extraction is considered to be complete when the ether phase is colorless.[3]

Table VII. Selection of Wavelength for Lanthanum Evaluation

Element	*Concentration γ/ml*	*Luminous intensity, % T*	
		440 mμ	*565 mμ*
Lanthanum	1000	43.5	105
Iron	100	0.6	10
Magnesium	1000	2.4	4
Thallium	1000	0	1.2
Gallium	100	0	0
Indium	10	0	0
Calcium	1000	7.5	>>100
Sodium	100	1.2	2.8
Lithium	1	0	0
Potassium	100	1.5	4.3
Rubidium	1000	5.4	10
Cesium	10	0	0
Barium	1000	4.8	32
Strontium	100	0.6	2.8

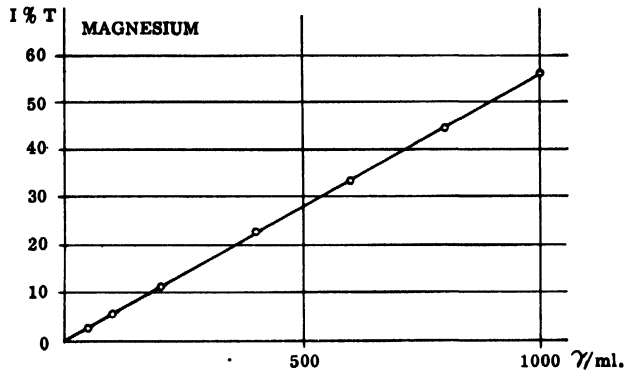

Figure 8

A special separation funnel was designed to enable the separation of the ether phase to be made without a pipette (Fig. 9); the operation thus being easy and clean. Before separating the ether phases, the funnel is inverted; 1 or 2 ml ether are added through *A*, and valve *B* is opened to rinse tube *C* to avoid losses of the aqueous phase.

After extraction of the uranium, the aqueous phase is transferred to a quartz precipiation vessel, rinsing the funnel and both stems.

The ether is evaporated by warming almost to dryness and the sample is then diluted to 25 ml, and transferred to a calibrated beaker.

Readings are taken at the correct wavelengths for each element; the intensity values obtained (expressed in % *T*) are compared with those obtained

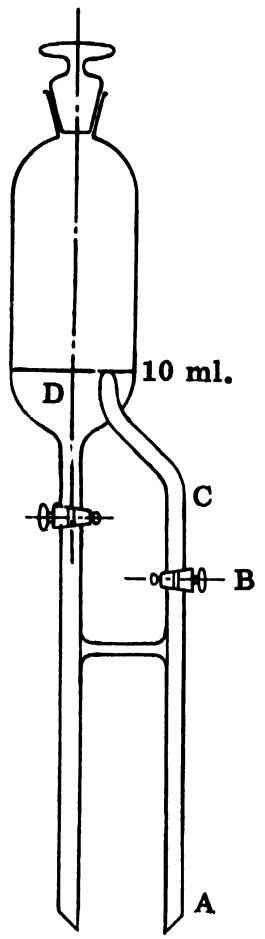

Figure 9

Table VIII. Interferences

λ, mμ	Element	Luminous intensity, in % T, produced by													
		Mg 1000 γ/ml	Fe 100 γ/ml	Tl 1000 γ/ml	Ga 100 γ/ml	La 1000 γ/ml	In 10 γ/ml	Ca 1000 γ/ml	Na 100 γ/ml	Li 2 γ/ml	Sr 100 γ/ml	K 100 γ/ml	Rb 1000 γ/ml	Cs 10 γ/ml	Ba 1000 γ/ml
371	Magnesium	50	0.2	0	0	0	0	0.6	0	0	0	0	0	0	0
372	Iron	22	1.7	0.2	0	0.6	0	1.1	0.3	0	0.2	0.2	1.4	0	0.1
377.6	Thallium	7.8	0	62	0	0.2	0	0.3	0	0	0	0	0.1	0	0
417.2	Gallium	0	0	0	3.0	0.1	0	0.5	0.1	0	0	0.1	0.4	0	0
440	Lanthanum	0.2	0.8	0	0	15	0	2.5	0.4	0	0.2	0.5	1.8	0	1.6
451.1	Indium	0	0	0	0	0.5	0.8	0.4	0.1	0	0.1	0.1	0.6	0	0.8
554	Calcium	0	0	0	0	0	0	13	0	0	0	0	0	0	0
589	Sodium	0	0	0	0	0	0	0.8	18	0	0	0	0	0	0
670.8	Lithium	0	0.2	0	0	0	0	2.4	0	5.7	1.7	0	0	0	0.7
681	Strontium	0	0	0	0	0	0	0.8	0	0	5.4	0	0	0	0.5
768	Potassium	0	0	0	0	0	0	0	0	0	0	6	0	0	0
780	Rubidium	0	0	0	0	0	0	0	0	0	0	0	21.0	0	0
852	Cesium	0	0	0	0	0	0	0	0	0	0	0	0.3	1.7	1.5
873	Barium	0	0	0	0	0	0	0.7	0	0	0	0	0	0	2.7

Table IX. Interferences

λ, mμ	Element	Mg 200 γ/ml	Fe 40 γ/ml	La 200 γ/ml	Sr 40 γ/ml	Ba 400 γ/ml
460.7	Strontium	0	0	0	97	5
515	Barium	0.5	1.1	1.4	0.9	26

with standard solutions (read simultaneously) and corrections are made for the interferences.[3]

Separation of Iron

If the sample contains iron, 20 ml of the initial solution are transferred to a precipitation vessel and evaporated almost to dryness; 0.5 ml redistilled hydrochloric acid are added; evaporation is repeated and the solution is transferred to the separation funnel with 5–7 ml 6*M* hydrochloric acid.[12]

Extraction is made with ether saturated with hydrochloric acid. In this form, the iron passes quantitatively to the ether phase (and together with it gallium, thallium, and a portion of the indium).[12,13]

The separation of the phases should be done carefully, since they emulsify easily. The funnel used is similar to the one described above.

The ether phase is evaporated, and made up to 10 ml with redistilled water. It is used for the study of iron (and if so desired, of gallium and thallium).

If the iron content is very high (it would have interfered in the previous readings) the aqueous phase also is evaporated almost to dryness and made up to 10 ml with redistilled water. Lanthanum and magnesium are studied in it (and, if required, the other elements).

Tables XI and XII contain the data obtained from the ether extractions in the nitric and hydrochloric acid media.

Table X. Influence of Acids*

λ mμ	Elements	Conc. HCl, ml/ml	Conc. HNO_3, ml/ml	Intensity, %T
372	Iron (100 γ/ml)	—	—	13
372	Iron (100 γ/ml)	0.01	—	14
372	Iron (100 γ/ml)	0.2	—	18
372	Iron (100 γ/ml)	—	0.01	13
372	Iron (100 γ/ml)	—	0.2	15.5
372	— —	0.2	—	0.7
372	— —	—	0.2	0.7
372	— —	0.8*	—	0.4
372	— —	—	0.8*	0
440	Lanthanum (200 γ/ml)	—	—	12
440	Lanthanum (200 γ/ml)	0.01	—	12
440	Lanthanum (200 γ/ml)	0.2	—	17.5
440	Lanthanum (200 γ/ml)	—	0.2	0.7
440	— —	0.2	—	0.7
440	— —	—	0.2	1.–
440	— —	0.8*	—	0.3
440	— —	—	0.8*	0.2
371	Magnesium (400 γ/ml)	—	—	22.5
371	Magnesium (400 γ/ml)	0.2	—	24
371	Magnesium (400 γ/ml)	—	—	20
371	— —	0.2	—	0.9
371	— —	—	0.2	0.7
371	— —	0.8*	—	0.6
371	— —	—	0.8*	0.4

*8 ml of each acid were evaporated to almost dryness, dissolved in redistilled water and made up to 10 ml in a graduated beaker.

Table XI. Recovery of Lanthanum, Iron and Manganese during Uranium Extraction with Ether from a Nitric Acid Medium

Series	Element	Amount added, mg/ml	Amount found, mg/ml
1	Lanthanum	0.48	0.46
	Iron	0.81	0.81
2	Lanthanum	0.21	0.21
	Iron	0.47	0.49
	Magnesium	0.20	0.20
3	Lanthanum	0.20	0.19
	Magnesium	0.20	0.20
4	Iron	0.16	0.16
5	Lanthanum	0.050	0.043
	Iron	0.050	0.050

Table XII. Extraction of Iron from the Chloride Mixture with Ether in Hydrochloric Acid Medium*

Sample	Amount added, mg/ml	Amount found, mg/ml
1	0.47	0.50
2	0.49	0.49
3	0.49	0.51
4	0.49	0.49
5	0.49	0.49
6	0.49	0.49
7	0.100	0.100
8	0.050	0.048

* The conditions of sensitivity and slit width depended on the concentration of the elements to be evaluated.

CONCLUSIONS

A study of the possibility of evaluating lanthanum, iron and magnesium by flame spectrophotometry has been made.

(*a*) The emission spectra of these elements were obtained with oxyacetylene and hydrogen-oxygen burners.

(*b*) The variables affecting the results (operating conditions of the instrument) were studied.

(*c*) The linear response of the luminous intensities of the concentrations was checked within the limits of the concentrations studied.

(*d*) The mutual interferences of these three elements were determined as well as the interferences caused by alkali metals, alkaline earths, gallium, indium and thallium.

(*e*) The method used is described.

(*f*) The recovery of lanthanum, iron and magnesium during the separation of uranium from a nitric acid medium is demonstrated.

Tables containing the experimental data obtained are included.

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Spectrophotometric Determination of Uranium with Thiocyanate in Acetone-Ethyl Acetate-Water Medium

By Oscar A. Nietzel and Michael A. DeSesa,* USA

Prior to the development of the method presented in this paper, uraniferous liquors containing more than 5 grams U_3O_8 per liter were analyzed in this laboratory by a conventional volumetric method based on reduction in a lead reductor to uranium (IV) and oxidimetric titration with cerium(IV) using ferroin indicator.[1] Any cations which could be reduced in the reductor had to be removed by a preliminary cupferron separation. Any organic material remaining had to be destroyed by fuming with perchloric acid. Solutions containing no other reducible cations could be reduced and titrated rapidly, but if nitrate ion was present, this also had to be destroyed by fuming with sulfuric acid. Thus, only a limited number of samples could be analyzed without a preliminary time-consuming removal of interferences.

With an increasing analytical load, the need for a more rapid method became apparent. Spectrophotometry seemed to offer the best possibility, since a survey of the literature revealed that many spectrophotometric procedures had been proposed and used for the determination of uranium. The literature on the analytical chemistry of uranium has been summarized very adequately elsewhere [2,3] and therefore will not be presented here. The method of Crouthamel and Johnson,[4] based on the yellow uranium thiocyanate complex in acetone, appeared to be as sensitive as any other but at the same time seemed rapid and not subject to many serious interferences.

When the thiocyanate-acetone method was tested on solutions of uranium with no interfering cations present, excellent analyses were obtained. However, when leach liquors from the ores commonly processed in this laboratory were analyzed, it became obvious that a separation of the uranium was necessary in order to obtain accurate results. The cations which have been reported[4,5,6] to interfere to any serious degree with the thiocyanate method in aqueous and acetone media are Fe(III), Mo(V), Pb(II), Ru(III), Co(II), Ni(II), Cr(III), Hg(II) and Cu(II). The tolerable limits for these cations were not exceeded in the usual leach liquors which were analyzed at this site. Further investigation revealed that vanadium and titanium are much more serious interferences than any one of those previously reported. After this work was initiated, two other references [7,8] to the interference of vanadium were noted, and spectrophotometric methods have since been reported for the determination of vanadium and titanium based on their thiocyanate complexes in an acetone-water medium.[9] Because titanium and especially vanadium may be constituents of uranium ores, it became necessary to devise a rapid means of separating vanadium and titanium from uranium before the thiocyanate-acetone method could be used.

The present paper reports a spectrophotometric procedure for all solutions, except those containing more than 2 grams of vanadium and 1 gram of titanium per liter. The method consists of extraction of the uranium from an aluminum nitrate medium into ethyl acetate followed by color development on a portion of the ethyl acetate extract with a saturated solution of ammonium thiocyanate in 67% acetone–33% water. Also presented is a special technique for samples containing up to 5 grams of titanium per liter involving a preliminary precipitation of the titanium in the extraction vial with *p*–hydroxyphenylarsonic acid.

APPARATUS

All quantitative measurements were made on the Beckman Model DU Spectrophotometer using matched one cm. Corex cells. A brief study was made to determine if a Coleman Model 14 Universal Spectrophotometer could be used for routine analysis, but a linear calibration curve could not be obtained with this instrument except at low concentration levels.

Screw cap vials, 4¼ in. long and 1 in. in diameter, and tin foil lined caps, S. A. Ansell and Sons, Inc., Boston, Mass. The screw caps are discarded after use.

Automatic 15 and 20 ml pipets, E. Machlett and Sons, New York.

Automatic shaker, Eberbach and Son Co., Inc., Ann Arbor, Michigan which has a special wooden platform built on it to hold about 27 vials in a horizontal position.

REAGENTS

Stannous Chloride, reagent grade, Baker and Adamson. Ten grams dissolved in 10 ml of concentrated hydrochloric acid, diluted to 100 ml and filtered through No. 42 Whatman paper.

Aluminum nitrate, reagent grade, Fisher Scientific Company.

* National Lead Company, Inc., Raw Materials Development Laboratory, Winchester, Massachusetts.

Acetone, reagent grade, Fisher Scientific Company.

Ammonium thiocyanate, reagent grade, Baker and Adamson. (Another manufacturer's reagent was also tested but it gave an unstable blank).

The color developing reagent consisted of 69 grams of ammonium thiocyanate dissolved in 66 ml of acetone, 23 ml of water and 10 ml of 10% stannous chloride reagent. The reagent should be just saturated in ammonium thiocyanate at room temperature. Since heat is absorbed during the dissolution process, the mixture was heated under the hot water tap in order to reach saturation rapidly. The reagent was prepared no more than one hour before use, but it is stable for at least three hours.

Standard solutions were prepared from National Bureau of Standards U_3O_8, NY–ST, dissolved in perchloric acid.

RECOMMENDED PROCEDURE

An aliquot of the sample (no more than 3 ml) containing 0.30 to 15 grams of U_3O_8 per liter is transferred into a 40 ml screw cap vial. Approximately 15 ml of saturated aluminum nitrate solution are added, followed by exactly 20 ml of ethyl acetate. The vial is capped and shaken for one minute. The ethyl acetate and water layers are completely separated by centrifugation. Ten ml of the ethyl acetate layer are pipetted into another vial and 15 ml of the thiocyanate reagent are added to the ethyl acetate. The final solution is mixed and the absorbance is measured within 15 minutes. The blank is prepared in the same manner as the samples. The absorbance is measured at 375 mμ (slit width, 0.16 mm) or if the absorbance is greater than 1.0, the reading is taken at 420 mμ slit width, 0.060 mm).

For samples which are known to contain titanium, 2 ml of a saturated solution of *p*-hydroxyphenylarsonic acid are added to the extraction vial and the solutions are allowed to remain overnight before they are extracted.

EXPERIMENTAL

Absorption Spectra

The absorption spectra of uranium, titanium, and vanadium in the thiocyanate-acetone medium are presented in Fig. 1. These solutions were developed according to the standard thiocyanate-acetone procedure.[4] Crouthamel and Johnson have reported[4] that absorbance measurements should not be made below 375 mμ because uranium and several other ions fluoresce in this region of the spectrum. Our own experience has been that measurements below 375 mμ are definitely more erratic than at longer wavelengths and very wide slit widths are required to zero the instrument. However, reproducible calibration data which obey Beer's Law were obtained for uranium at 375 and 420 mμ, and presumably could be obtained at any other wavelength in this region.

While there is no apparent absorption peak in the visible region of the spectrum for uranium in a thiocyanate-acetone medium, vanadium and titanium exhibit peaks at 398–400 mμ and 416–420 mμ respectively. The intensely yellow vanadium thiocyanate complex is formed only in the presence of a reducing agent and was demonstrated to contain trivalent vanadium. In the absence of a reducing agent, tetravalent vanadium gives a deep blue color with thiocyanate and pentavalent vanadium gives no color change. Since stannous chloride is added during the

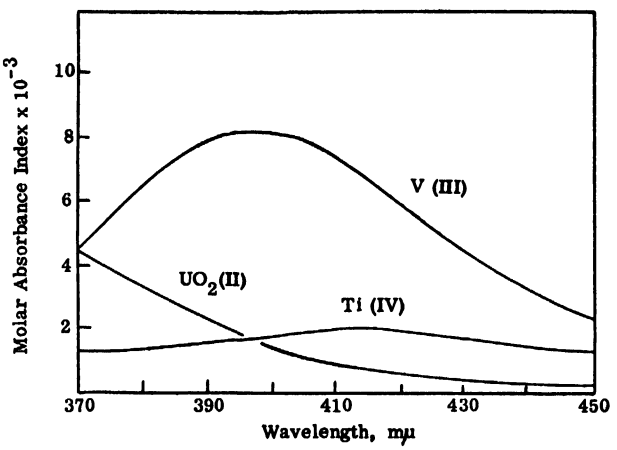

Figure 1. Absorption spectra of uranium, vanadium, and titanium in thiocyanate medium

recommended procedure to reduce traces of iron, any vanadium also present will be reduced. From the spectral data presented in Fig. 1, it is apparent that both vanadium and titanium interfere with the determination of uranium.

Separation Studies

The conventional cupferrate extraction method for purifying uranium solutions involving preliminary oxidation with permanganate, precipitation of the cupferrate, extraction into chloroform and destruction of the organic matter in the aqueous phase was tried on mixtures of uranium, iron, and vanadium. Some typical results are shown in Table I. Some vanadium remained and was responsible for the high results in the last four mixtures. However, when solutions containing vanadium alone underwent the cupferrate extraction, perfectly blank solutions were obtained. The failure to completely remove the last traces of vanadium from mixtures of uranium and vanadium may possibly be ascribed to the formation of a uranyl vanadate complex.

The extraction of uranium from a nitrate medium into ethyl acetate was also examined as a possible means of separating uranium from interferences. Other workers[4,10] who used this technique for separation prior to spectrophotometric analysis used three extractions into ether followed by evaporation of the organic phase over water to recover the uranium. It has been our experience in this laboratory that one extraction from a mixture of one or two ml of sample and 15 ml of saturated aluminum nitrate into ethyl acetate provides complete extraction for uranium in determinations by a fluori-

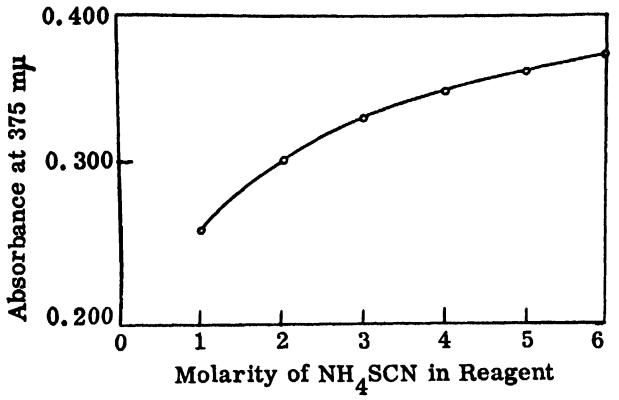

Figure 2. Color development as a function of ammonium thiocyanate concentration in the reagent

metric method. Since ethyl acetate is miscible with acetone, the following procedure was proposed and tested:

To an aliquot of no more than two ml of sample in a 40 ml screw cap vial, 15 ml of saturated aluminum nitrate were added followed by 20 ml of ethyl acetate. The vial was shaken for one minute and centrifuged to separate the phases. Ten ml of the organic phase was transferred into another vial. Fifteen ml of a saturated ammonium thiocyanate, 0.4% stannous chloride solution in acetone was added. The solution was mixed and the color measured against a blank prepared in the same manner as the sample. With this procedure a linear calibration curve was obtained, and the mixtures of uranium, iron and vanadium previously mentioned were analyzed rapidly and accurately.

Color Development Reagent

Two refinements involving the color developing reagent were made. The ammonium thiocyanate was dissolved in a mixed acetone-water solvent to prevent a troublesome precipitation of salts in the acetone-ethyl acetate mixture. Tests showed that the acetone to water ratio must be at least two to one for the solution to be miscible with ethyl acetate. Further experimentation showed that the higher the water concentration in the reagent, the more ammonium thiocyanate could be dissolved. Therefore a mixture of 67% acetone and 33% water was chosen as the solvent for the ammonium thiocyanate reagent. As indicated under the description of reagents, part of the aqueous phase is added as 10% stannous chloride so that in every 15 ml aliquot of the color developing reagent one ml of 10% stannous chloride is present.

Table I. Cupferron Separation of Mixtures

Taken, mg			*Found, mg*
U_3O_8	*Fe(III)*	*V(V)*	U_3O_8
0.500	1.01	—	0.498
0.500	2.02	—	0.504
0.500	—	0.966	0.536
0.500	—	1.93	0.666
0.500	1.01	0.966	0.585
0.500	2.02	1.93	0.750

A study was made to determine the optimum thiocyanate concentration in the 67% acetone–33% water solvent. In this experiment, 10 ml aliquots of an ethyl acetate solution containing 0.05 grams of U_3O_8 per liter as uranyl nitrate and 15 ml of 67% acetone–33% water solutions of various concentrations of ammonium thiocyanate were mixed and the resulting color intensity determined against a corresponding blank. The results of this study are shown in Fig. 2. A six molar solution of ammonium thiocyanate in 67% acetone–33% water solvent is a saturated solution, and is the obvious choice as the color developing reagent since it yields the most intense color which is least affected by small changes in ammonium thiocyanate concentration.

Optimum Conditions for Extraction

Using the recommended procedure, a study was made to determine how large a volume of sample could be taken before the dilution of the aluminum nitrate salting agent became serious enough to cause incomplete extraction. Negligible error was found for aliquots up to 3 ml, but analyses of 4 and 5 ml aliquots were low by 1.0 and 2.4% respectively. If the sample aliquot was saturated with solid aluminum nitrate, the error on a 5 ml aliquot was only 0.5%. It is recommended that, if a solution is so dilute that an aliquot larger than three ml must be taken, the aliquot itself be saturated with solid aluminum nitrate before the salting agent is added.

A factorial experiment was designed to test three variables, namely, acidity of the sample, volume of the nitrate salting agent and composition of the salting agent. Each factor was studied at three levels. The sample was made up in 1*M* sodium carbonate, 0.05*M* nitric acid and 1.0*M* nitric acid. The volume of the salting agent was 5, 10 and 15 ml. The salting agents were saturated aluminum nitrate with 0, 5 and 10% by volume of added nitric acid. The data was collected in nine sets of three samples in each set measured against a blank prepared from the same volume and composition of salting agent. The data are tabulated in Table II and summarized in the form of two-way tables in Table III. Duplicates were not run because enough information was available without further statistical analysis.

An examination of the two-way tables leads to certain conclusions. For a wide range of acidity in the sample there is less than a 2% range in the average absorbance values. Therefore, either the acidity of the sample is unimportant or the buffering action of aluminum nitrate neutralizes excess acid or base. Adding nitric acid to the nitrate salting agent apparently decreases the efficiency of the extraction, but this effect may be due to a dilution of the ethyl acetate phase by nitric acid. In any case, saturated aluminum nitrate was the choice as the salting agent. Finally, the actual volume of salting agent need be only approximately 10–15 ml since the average absorbance values for 5, 10 and 15 ml are almost identical.

Stability in Color

The yellow color of the uranyl thiocyanate complex in the ethyl acetate-acetone-water medium developed at once, was stable for at least 10 minutes and then increased in intensity slightly with time. The increase amounted to 1.4% in one-half hour and 3% in an hour.

Table II. Absorbance Data for Factorial Experiment on Extraction Variables

Salting agent % $Al(NO_3)_3$-HNO_3	*Volume of salting agent, ml*	*1.00 gram U_3O_8 per liter made up in*		
		1M Na_2CO_3	*0.05M HNO_3*	*1M HNO_3*
100–0	5	0.325	0.332	0.338
100–0	10	0.340	0.345	0.344
100–0	15	0.342	0.344	0.342
95–5	5	0.330	0.332	0.333
95–5	10	0.333	0.336	0.332
95–5	15	0.326	0.331	0.333
90–10	5	0.329	0.335	0.335
90–10	10	0.309	0.337	0.321
90–10	15	0.340	0.340	0.303

Calibration Data

Since the method has been put into routine operation, a set of standards has been included with each batch of samples. Thus, any changes in the absorbance index due to a change in reagents, cell blanks, operator technique or some other factor could be immediately detected. However, thus far the absorbance index has remained essentially constant. For 17 calibrations, the average absorbance index at 375 mμ varied between 0.354 to 0.364, the overall average was 0.360 and the coefficient of variation was ±0.72%. The absorbance index is in such units that one ml of a 1.00 gram U_3O_8 per liter solution put through the recommended procedure gives an absorbance of 0.360.

Although slight changes are observed in the absorbance index, the analysis of any one sample is reproducible from day to day. Therefore, it seems that the slight variation in the absorbance index is due to minute differences in the instrument settings which in this instance are significant since the absorbance measurements are made on a steep portion of the absorption curve.

Interferences

The possible interference of carbonate, phosphate and sulfate in the extraction was evaluated, and it was found that at least a one molar concentration of each ion may be tolerated with no ill effect.

The extent of separation of uranium from the various cations reported to interfere in the thiocyanate method was also determined. Synthetic mixtures containing 0.50 mg U_3O_8 and 100 mg each of Co(II), Cr(III), Cu(II), Fe(III), Hg(II), Mo(VI), Ni(II) and Pb (II) in a volume of three ml were carried through the standard procedure. Only Ni(II) and Pb(II) interfered causing positive errors of 2.4% and 3.0% respectively. Since such large concentrations of these elements are unlikely, the present procedure is not subject to the interferences previously mentioned in other variations of the determination of uranium as the yellow thiocyanate complex.

When the interference of vanadium was tested according to the same procedure as the other elements, a precipitate of what appeared to be V_2O_5 was formed upon the addition of the aluminum nitrate. This precipitate occluded some of the uranium. Therefore a more detailed study of the possible interference of vanadium was made. It was found that up to 2.0 mg of vanadium(V or IV) in the sample aliquot caused a maximum positive absorbance error equivalent to only 0.02 mg of U_3O_8. However, larger amounts of vanadium(V) were precipitated in the extraction vial and occlude uranium. Larger amounts of vanadium(IV) caused proportionately increasing errors so that above 2 mg of vanadium(IV) each mg in the sample aliquot was equivalent to 0.01 mg of U_3O_8.

Titanium is partially extracted from aluminum nitrate into ethyl acetate and forms a yellow orange thiocyanate complex with the color developing agent. However, the interference of titanium can be eliminated by adding two ml of a saturated solution of *p*-hydroxyphenylarsonic acid to the sample aliquot in the extraction vial and allowing the titanium to precipitate. The leach liquors derived from certain ores evidently contained a stable titanium complex for it was found necessary to allow these samples to stand overnight with the precipitating agent before the titanium was removed to such an extent that it no longer interfered.

Results

In order to test the method as developed, about 50 samples were picked at random and analyzed by the spectrophotometric method. These samples had been previously analyzed by fluorimetric and macro- and microvolumetric methods. The average per cent deviation of the spectrophotometric analysis from the other methods of analysis was as follows: from macrovolumetric, ± 1.0%; from fluorimetric, ±1.7%; from microvolumetric, ±2.0%.

As an example of the type of accuracy obtainable by this method, the comparative analyses are shown in Table IV on four ore residues and three uranium concentrates submitted for umpire analysis to this laboratory.

DISCUSSION

The method reported in this paper has replaced the volumetric method previously used in this

Table III. Two-Way Tables for Extraction Variables

Sample type	*1M Na_2CO_3*	*0.05M HNO_3*	*1M HNO_3*
Average absorbance	0.331	0.337	0.331
% HNO_3 in salting agent	0	5	10
Average absorbance	0.339	0.332	0.328
Volume of salting agent, ml	5	10	15
Average absorbance	0.332	0.333	0.333

Table IV. Comparative Analyses

Sample		%U_3O_8 Fluorimetric	Volumetric	Spectrophotometric	Average
Residue	1	0.263	0.262	0.264	0.263
	2	0.254	0.252	0.252	0.253
	3	0.235	0.232	0.238	0.235
	4	0.402	0.404	0.400	0.402
Concentrate	1		74.1*	74.2	
	2		72.4*	73.0	
	3		72.9*	73.1	

* Average of volumetric results obtained from two other laboratories.

laboratory. Samples containing at least 0.10 gram U_3O_8 per liter may be analyzed rapidly and with satisfactory accuracy. Because of the sensitivity of the method, some of the samples previously analyzed by a fluorimetric procedure are now analyzed by the spectrophotometric procedure. A team of two men can analyze about 80 samples a day, and introduction of the method has resulted in a considerable increase in the capacity of the analytical laboratory.

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Spectrophotometric Determination of Microquantities of Beryllium with *p*-Nitrobenzene-Azo-Orcinol

By J. L. Huguet and A. Aguiló,* Argentina

PART I: PURIFICATION OF DYE

The determination of the beryllium content of the atmosphere in the laboratories and plants which work with the metal and its compounds is of the utmost importance, due to its high toxicity.[3,10,18,22]

In 1950, the Atomic Energy Commission of the United States recommended a maximum limit of 2 γ of beryllium per cubic meter of air as an average concentration for an eight hour work day.

The estimation of such small quantities can be carried out by colorimetric methods,[1,2,5,7,24,29,31] fluorimetry[8,12,16,34] and spectrography.[6,20,21,26]

Among the colorimetric reagents, we selected *p*-nitrobenzene-azo-orcinol because of its specificity and high sensitivity, which is 0.005 per cm^2 for an optical density of 0.001.[23]

This compound was synthetized and used for the first time in the identification of beryllium in the year 1934.[15] Thereafter, it was used for the investigation[13,14] and photometric determination[19,28] of beryllium in minerals and alloys. The determination was made adding the dyestuff, dissolved in 0.10*N*, sodium hydroxide, to a solution of beryllium in a buffer solution made up of sodium hydroxide and boric acid, and then measuring the optical density of the solution, with respect to a suitable blank, at a wavelength of approximately 514 mμ.

While using the method, it was found that the slope of the calibration curve changed from one batch of dyestuff to the next. This was due to the fact that the reagent was not pure, and that, under normal colorimetric conditions, an excess of coloring matter is not sufficient to reach the range in which the optical density becomes independent of it. By working in this region, the blank extinction would be very high. It was found that the purity of the dyes used was 31% and 60% respectively, and that a fraction of the impurities was not soluble in a 0.10*N* solution of sodium hydroxide.

The fraction of the dyestuff soluble in this medium was then isolated. Starting from this fraction, the purity of which was approximately 70%, the pure dye could be obtained by recrystallization from methyl alcohol.

The purity criteria were provided by chromatography on alumina and spectrophotometry of the complex formed with beryllium.

Experimental Part

Equipment and Reagents

Spectrophotometer: all spectrophotometric determinations were made with a Unicam S.P. 500 spectrophotometer.

Alumina: in the chromatographic tests, Merck alumina was used for the quantitative adsorption analysis according to the Wislicenus method, and, also the Merck product for the adsorption analysis according to Brockmann.

Solvents: all the solvents used for chromatography and crystallization were purified by conventional techniques.[32]

p-nitrobenzene-azo-orcinol: B.D.H. "spot test reagent," and Hopkins and Williams "organic reagent for metals."

Standard solution of beryllium I (400 γ of beryllium per ml): 1.108 gm of spectrographically pure beryllium oxide, previously heated to constant weight at 1000°C, then transferred to a leacher, 5 ml of sulfuric acid pa ($\delta = 1.84$) is added, and the whole is heated on a sand bath until complete elimination of the excess acid. This is allowed to cool off, 100 ml of distilled water and 5 ml of sulfuric acid pa ($\delta = 1.84$) are added, the whole is heated until total dissolution, and made up to one liter with distilled water.

Standard solution of beryllium II (100 γ of beryllium per ml): 0.277 gm of beryllium oxide are treated in the same manner as just described.

Standard solution of beryllium III (10 γ of beryllium per ml): prepared when and as needed by dilution of the solution mentioned above.

Explanations

All the dyestuff solutions used for the spectrophotometric determinations, except in the cases in which the method of preparation is indicated, were obtained by stirring the finely ground dye in the 0.10*N* sodium hydroxide for three hours, bringing it up to volume with 0.10*N* sodium hydroxide, and then filtering on a Büchner funnel (with two filter papers, one SS 589[3] and the other Whatman 54).

Original language: Spanish.

* Comisión Nacional de la Energía Atómica.

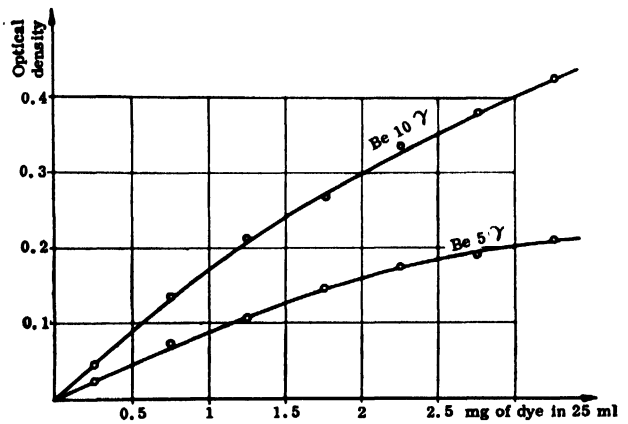

Figure 1. Influence of the amount of the reagent on the colorimetry

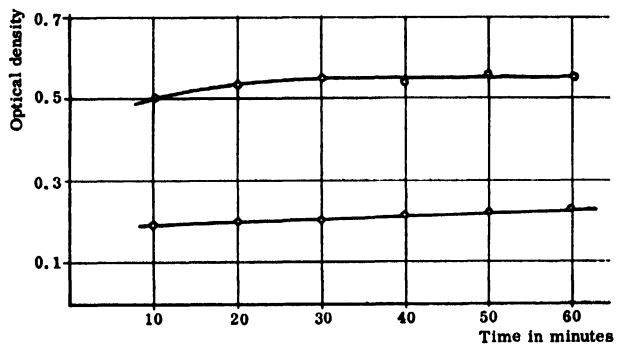

Figure 2. Extraction of the dye with 0.1N NaOH. Curve I: beryllium complex with respect to the blank. Curve II: dye, with respect to water

The pure dyestuff fractions "soluble in sodium hydroxide," were dissolved in 0.10*N* sodium hydroxide and the volume was made up with the same solution.

When the weight of "crude" dye used in the spectrophotometric determinations is given, this refers to the quantity which one would have in the same number of milliliters of solution added, if the dyestuff were totally soluble.

In all these determinations, the order in which the reagents were added was: (1) sodium hydroxide 2*N*; (2) standard beryllium solution; (3) boric acid 0.64*M*; (4) dye solution; (5) water, to make up final volume.

The sodium hydroxide indicated includes that which is added to the dye solution and to the solutions to which a standard solution of beryllium was added including the amount of sodium hydroxide required to neutralize the sulfuric acid present in the solution.

Influence of Reagent Concentration on Results of Spectrophotometry

Solutions having a final volume of 25 ml, and which contained 3 ml of 2*N* sodium hydroxide, 5 ml of 0.64*M* of boric acid, 1.00 or 2.00 ml of the standard solution of beryllium sulfate (10 γ of Be per ml) were prepared, as well as variable quantities of a solution of B.D.H. (0.25 mg per ml) dyestuff.

The optical density of the above mentioned solutions was determined at a wavelength of 525 mμ, in 2 cm cells, with respect to blanks identical to those used for the solutions, but without beryllium.

The results are shown in Fig. 1.

Sodium Hydroxide Soluble Fraction Extraction

One gm of Hopkins and Williams dyestuff, finely ground, was transferred to a 2-l vessel, 1 l of 0.10*N* sodium hydroxide solution was added, and continuous stirring was kept up. Every 10 minutes, 20-ml samples were taken out and filtered. From the filtrates, 10.0 ml were taken and diluted to 50.0 ml with 0.10*N* sodium hydroxide.

Determinations were made of the optical density of the beryllium complex with respect to the blanks, as well as of that of the blanks with respect to water, in 1-cm cells, at a wavelength of 514 mμ. The solutions contained, in a final volume of 25 ml, 3.00 ml of 2*N* sodium hydroxide, 5.0 ml of 0.64*M* boric acid, 2.5 ml of standard beryllium solution (400 γ of beryllium per ml), and 3.75 ml of the dyestuff solutions prepared earlier.

The results shown of Fig. 2 indicate that the beryllium-sensitive fraction is totally dissolved at

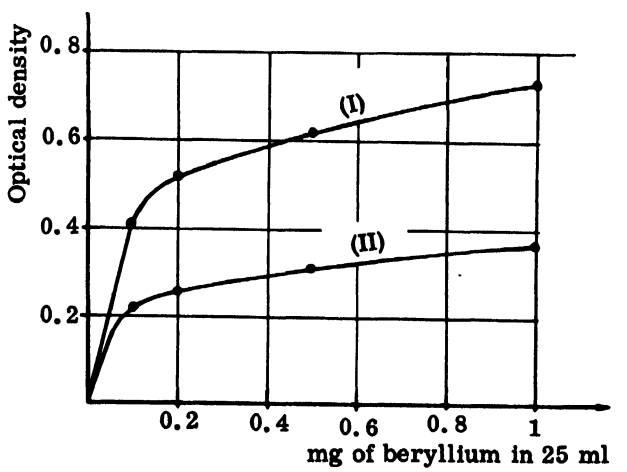

Figure 3a. Curve I: 1 mg of dye in 25 ml. Curve II: 0.5 mg of dye in 25 ml

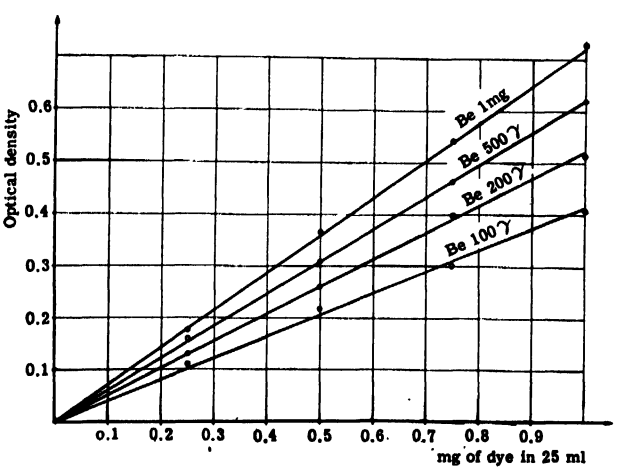

Figure 3b. Estimation of the dye. Selection of the beryllium concentration

the end of thirty minutes, and that longer stirring merely increases the amount of impurities extracted, as shown by the values obtained for the blanks.

Preparation

The finely ground dyestuff was placed in a vessel and 0.01*N* sodium hydroxide added. Stirring was kept up for thirty minutes, and filtration then took place on double filter paper, one SS 589[3] and another Whatman No. 54. The filtrate was neutralized with 1*N* hydrochloric acid and an excess of 2 ml added.

The dye precipitated in the form of reddish flakes which were filtered on a Jena 25 G.4 plate or Büchner funnel, using SS 589[3] paper. The mother liquor was slightly yellowish, and this was not appreciably intensified by the presence of an alkali, showing that precipitation was nearly complete.

The precipitate was washed three times with distilled water and the plate or paper was placed in a stove at 80°C. After one hour approximately, the precipitate could readily be taken off and partly ground and put in an oven held at 80°C until its weight was constant. The percentage of solubles thus obtained (without allowing for mechanical losses) varied from 33% to 35% for Hopkins and Williams and 70% to 83% for B.D.H. material.

Purity Criteria

The preliminary experiments carried out showed that the "soluble in sodium hydroxide" fraction could be separated into two parts using an activated cellulose column.

Only one of these two fractions is sensitive to beryllium, and it was shown that it also could be separated by adsorption on activated alumina[4, 30] which ruled out paper chromatography as a criterion of purity.

The chromatograms obtained on the alumina column according to Wislicenus, and on plain alumina according to Brockman, revealed four perfectly differentiated bands, which we call *A, B, C, D* starting from the base of the column.

Of the two alumina samples tested, we preferred the first since the fraction sensitive to beryllium shows a disturbing double-band effect in the other,[25, 27] and is affected by the alkalinity of this type of alumina.

In these experiments, use was made of columns 1.5 cm in diameter and 30 cm in height. The alumina was added, in suspension in a mixture made up of equal parts of acetone and benzene, in portions of 0.5 grams, each one of which was compacted with the help of slight air pressure: the height of the alumina was 15 cm. Each chromatogram was developed with 25 mg of a dyestuff dissolved in 10 ml of a mixture of acetone and benzene in the proportions mentioned before, and development was completed with 10 ml in a mixture of acetone and methanol in equal fractions.

The incorporation of the dye and its subsequent development were carried out with the help of a slight air pressure. Samples of the B.D.H. and

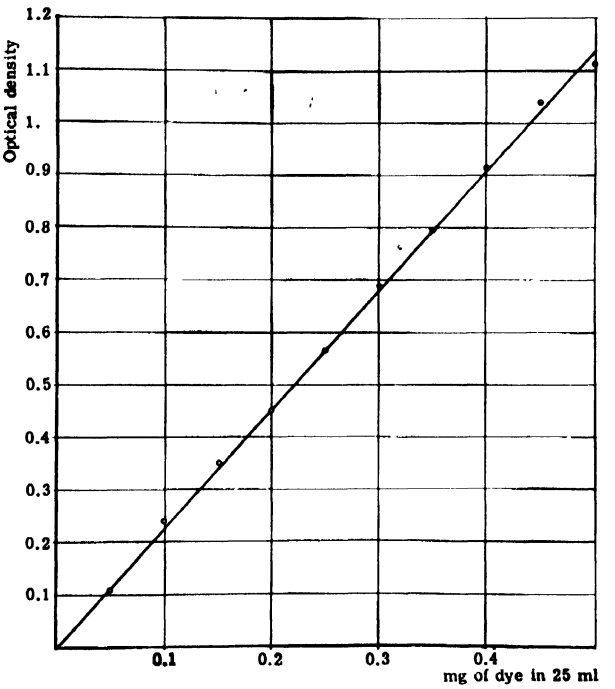

Figure 4. Estimation of dye. Calibration curve for pure dye

Hopkins and Williams dyes were analyzed, and the fractions also made up of "soluble in sodium hydroxide" materials.

The *A, B, C, D* bands, show up in all the samples tested, both in the presence of air and in a nitrogen atmosphere.

It will be observed that band *D* is wider in the Hopkins and Williams dye, while *A* and *C* are

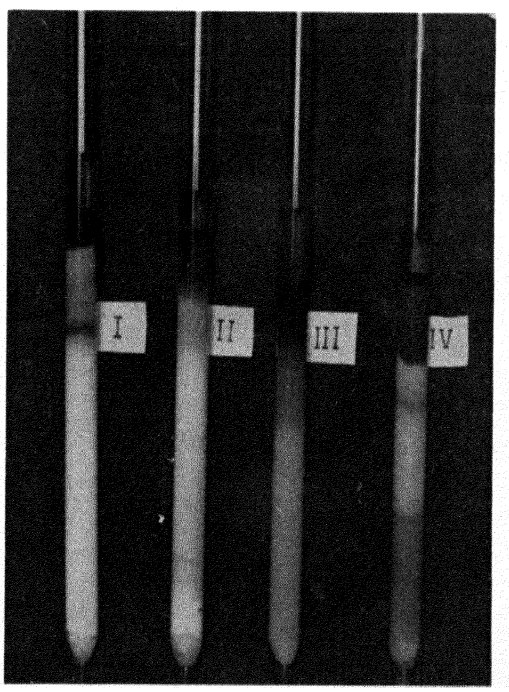

Figure 5. Adsorption of the "sodium hydroxide soluble" fraction of the Hopkins and Williams dye. I and III: Incorporated in acetone and benzene 50% solution; II and IV: developed with 50% acetone methanol solution. Adsorbent: alumina. I and II, according to Brockman; III and IV, according to Wislicenus

wider in the B.D.H. The same relationship was observed in the corresponding "sodium hydroxide soluble" fraction.

In Fig. 5, can be seen the chromatograms developed with 25 mg of the sodium hydroxide soluble fraction of the Hopkins and Williams dyestuff and alumina according to the Brockman method (I and II), and on alumina according to the Wislicenus technique (III and IV).

I and III show the appearance of the column immediately after the incorporation of the dye, and II and IV show it immediately after development.

The fractions corresponding to the *A*, *B*, and *C* bands were obtained by vacuum drying of the eluates.

In order to obtain fraction *D*, we separated the alumina occupied by this band. This alumina was agitated with 20 ml of 0.10*N* sodium hydroxide, it was filtered and the filtrate was neutralized with *N* hydrochloric acid, after which the precipitate obtained was centrifuged, washed and dried under vacuum, at 70°C.

With the four resulting fractions, a test was made on sensitivity to beryllium under the conditions set by the colorimetric method, using 1 mg of Be.

Only fraction *C* was sensitive, and when the chromatogram was developed with it, under the conditions mentioned above, a single band was obtained, looking and behaving just like the original *C* band.

Fraction *A* is completely insoluble in 0.10*N* sodium hydroxide, despite which it goes with the "soluble" dye in this medium (from which it was obtained) and its solutions in sodium hydroxide, which was verified by extracting it from them with benzene. This is probably due to its property of forming very fine suspensions, which are difficult to filter.

In keeping with the experiments mentioned above, it can be deduced that column chromatography with activated alumina as an adsorbent, can be used as a criterion of purity. On the other hand, purity is not adequate as a method of preparation of pure dye, since the beryllium-sensitive fraction is very strongly absorbed, and the quantities recovered are very small, but it can be used to eliminate the *D* fraction at an intermediate stage of purification.

Some of the fractions not sensitive to beryllium are formed from more than one substance, but their separation was of no interest for this work.

Spectrophotometry

Four series of four solutions were prepared. The solutions, in each series, contained in a final volume of 25.0 ml, 3.0 ml 2*N* NaOH, 5 ml of 0.64*M* H_3BO_3 and variable quantities of Hopkins and Williams reagent (0.25, 0.50, 0.75 and 1.00 mg). Each series contained, respectively 0.100, 0.200 and 0.500 mg of beryllium.

The optical density of the solutions with respect to identical blanks without beryllium was read in 1 cm cells, at a wavelength of 514 mμ.

The dye was added in a solution containing 0.25 mg per ml. In the series containing 0.100, 0.20 and 0.50 mg of beryllium it was added in a solution of 100 γ per ml, and in the series containing 1.00 mg, in a solution of 400 γ per ml.

Table I. Spectrophotometric Determination of the Purity of Various Dyes

Dye	Concentration (mg/ml)	Volume taken, (ml)	Mg of dye in volume taken	Optical density*	Optical density (mean)	Optical density (0.50 mg)
Hopkins and Williams, original	0.25	3.00	0.75	0.515 0.530 0.525	0.523	0.349
Hopkins and Williams, original	0.25	3.00	0.75	0.540 0.544 0.532	0.539	0.359
B.D.H., original	0.11	4.00	0.44	0.597 0.600 0.605	0.601	0.683
B.D.H., original	0.11	4.00	0.44	0.595 0.597 0.600	0.597	0.679
Hopkins and Williams, soluble 1	0.09	4.00	0.36	0.621 0.618 0.630	0.623	0.865
Hopkins and Williams, soluble 2	0.09	4.00	0.36	0.627 0.622 0.630	0.626	0.869
B.D.H., soluble 1	0.065	4.00	0.26	0.390 0.389 0.391	0.390	0.750
B.D.H., soluble 2	0.065	4.00	0.26	0.429 0.429 0.432	0.430	0.827

* The optical densities of column 5 were determined by taking aliquots of the solution of each dye; each one is the average of the three spectrophotometric readings.

Table II. Approximate Solubility of the Dye

Time, minutes	*Approximate temperature, °C*	*Optical density*	*mg dye in sample*	*Concentration, mg/ml*
10	20	0.22	0.10	1.0
30	20	0.22	0.10	1.0
10	65	1.14	0.50	5.0
30	65	1.10	0.48	4.8

It was proved that, with quantities of beryllium greater than 200 γ in 25.0 ml, the optical density of the complex formed with the dye is a linear function of the concentration of the latter and that, when the quantities are of the order of 1.00 mg in 25 ml, the optical density of the complex is nearly independent of the beryllium concentration.

Under these conditions, the spectrophotometric complex can be used as a quantitative criterion for the comparison of the various dye purities.

Two solutions in 0.10*N* sodium hydroxide were prepared, and each of the initial dyes and two of each of the relevant "sodium hydroxide" solubles. The latter were obtained from solubles prepared independently.

Three equal fractions were taken from each of the solutions, and a spectrophotometric determination was made, under conditions similar to those noted before, with 1 mg of beryllium.

The results are given on Table I.

From the optical densities referred to 0.50 mg of dyes (column 6, Table I), the following deductions can be made:

(*a*) The active principle content of the B.D.H. dye is approximately twice that of the Hopkins and Williams material.

(*b*) The substances soluble in sodium hydroxide are purer than the dyes, particularly in the Hopkins and Williams compound, in which the "sodium hydroxide" soluble portion contains 2.4 times more active principle than the original dye.

(*c*) The reproducibility of the "sodium hydroxide" soluble products is greater in the Hopkins and Williams dye than in the B.D.H. material due to the fact that, in the latter, the insoluble substances form suspensions which are difficult to filter out and mar its purity to variable extents.

The latter is confirmed by the fact that the soluble fraction of B.D.H. dye showed, in the chromatograms, a greater proportion of insolubles in 0.10*N* sodium hydroxide *A* fraction.

Crystallization

The following solvents were tested: acetone, benzene, petroleum ether and methyl alcohol, the latter having been adopted for reasons of solubility and ease of crystallization.

Crystallization from the original dyes was tried, as well as for the relevant "sodium hydroxide soluble" fractions, which showed that it is very difficult to obtain crystals with the former.

With the solvent selected, and starting from the "sodium hydroxide soluble" fraction of the B.D.H. dye, we obtained 250 mg of crystals, with which a calibration curve was drawn. This curve made it possible to determine the purity of the dyes, to determine the approximate solubility of the crystals, and to follow quantitatively the crystallizations.

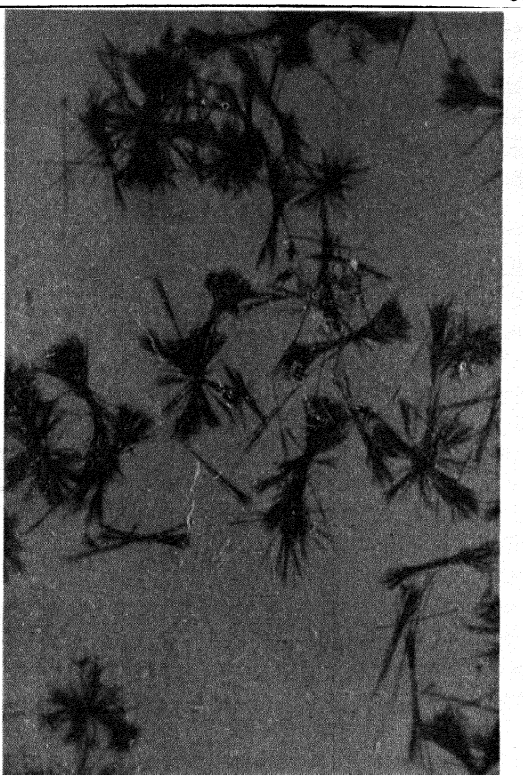

Figure 6a. Crystals of *p*-nitrobenzene-azo-orcinol. Slow cooling of a saturated solution at 65°C in methyl alcohol (150×)

Approximate Solubility of the Crystals

150 mg of crystals were placed in a 50-ml Erlenmeyer flask, 20 ml of methyl alcohol were added, a reflux condenser was fitted, and the solution was stirred by means of a magnetic agitator. Two samples of 0.10 ml were taken, one after 10 and the other after 30 minutes of agitation, by means of a pipette with SS 589[3] filter paper.

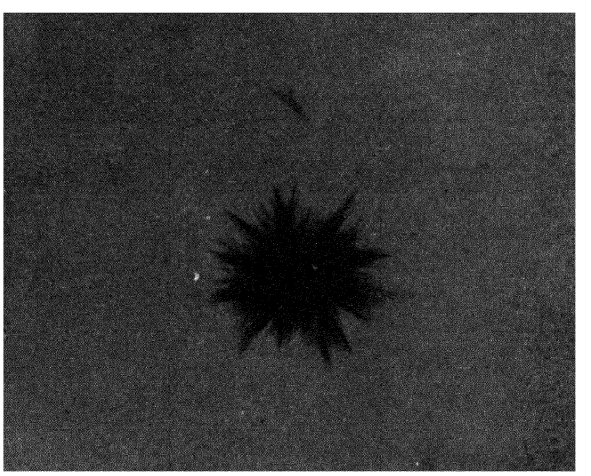

Figure 6b. Crystals of *p*-nitrobenzene-azo orcinol. Sudden cooling of a saturated solution at 65°C, in methyl alcohol (300×)

The optical density of the complex formed with beryllium by using 1 mg of beryllium and the dye sample taken was determined.

The operation was repeated by keeping the solution at the boiling point. The data will be found in Table II.

Crystallization of the B.D.H. Dye

400 mg of "sodium hydroxide soluble" B.D.H. dye, the purity of which was approximately 75%, were placed in a 100 ml Erlenmeyer flask. To this, 55 ml of methyl alcohol were added, a reflux condenser fitted, and the solution was brought to the boil while being stirred, and boiled for ten minutes. Filtration was carried out through a double thickness of SS 589[3] paper, and the solution was then gradually cooled to a temperature of −20°C, in a bath of methyl alcohol and dry ice. It was then taken out of the bath, keeping up the stirring until 0°C. The crystals obtained were centrifuged, and a sample of 0.10 ml of the mother liquor was used to determine the concentration of the active principle. This was found to be 1.2 mg per ml. The yield of crystallization was thus approximately 70%.

The crystals obtained were recrystallized from 40 ml of methyl alcohol, following the technique mentioned above. The concentration in the mother liquor of the active principle was 1.1 mg per ml, and the crystallization yield was 80%.

The crystals were dried in a vacuum giving a final weight of 140 mg.

Crystallization of Hopkins and Williams Dye

As with the fraction of dye soluble in sodium hydroxide in the case of the Hopkins and Williams material having a purity of approximately 75%, it was impossible to obtain crystals directly due to the tendency of the dye to precipitate in an amorphous form and to give supersaturated solutions.

This drawback was obviated by the absorption of some impurities (fraction D) in activated alumina before crystallization. To this end, 400 mg of the sodium hydroxide soluble fraction of the Hopkins and Williams dye were dissolved in 30 ml of acetone, and the solution was passed through a column 1.5 by 30 cm, which contained 3 gm of alumina activated according to the Wislicenus method. The solution was vacuum dried and from the fraction thus obtained, the dye was crystallized in the form mentioned above. This gave 135 mg of crystals.

The crystals obtained by this last technique were chromatographically pure, while those obtained by direct crystallization, starting from the sodium hydroxide soluble fractions of the B.D.H. dye still contained small amounts of fraction D. However, the impurities must be in a proportion of less than 2%, since both crystals gave the same results on being analyzed by the spectrophotometric method.

The crystals obtained by progressively cooling the solution are to be seen on Fig. 6*a*, and Fig. 6*b* shows those given by sudden cooling, which are clearer and of a lower apparent density.

Dosage of the Dye

An amount of 50.0 mg of the crystals obtained from the "soluble" fraction of the B.D.H. dye was dissolved in 500 ml of 0.10*N* sodium hydroxide.

A series of solutions containing in a final volume of 25.0 ml, 3.0 ml of 2*N* sodium hydroxide, 2.50 ml of beryllium (400 γ/ml), 5.0 ml of 0.64*M* boric acid

Table III. Estimation of the Dye

Dye	*mg in the volume taken*	*Optical density*	*Active principle per mg from calib. curve*	*Active principle, %*
Hopkins and Williams, original	0.75	0.523	0.230	31
Hopkins and Williams, original	0.75	0.539	0.237	32
B.D.H., original	0.44	0.601	0.265	60
B.D.H., original	0.44	0.597	0.263	60
Hopkins and Williams, soluble 1	0.36	0.623	0.275	76
Hopkins and Williams, soluble 2	0.36	0.626	0.274	76
B.D.H., soluble 1	0.26	0.390	0.175	67
B.D.H., soluble 2	0.26	0.430	0.190	73
Hopkins and Williams, crystals	0.26	0.589* 0.590* 0.591*	0.260	100

* These optical densities were determined taking various aliquots of the dyestuff solution; each one is an average of three spectrophotometric readings.

solution, and variable quantities of the dye, was prepared. The optical density with respect to blanks equal to the solutions mentioned above, but without beryllium, was measured in 1-cm cells at a wavelength of 514 mμ. From the values obtained in this way, a calibration curve was drawn (Fig. 4). Precisely the same method was used with the crystals obtained from the Hopkins and Williams dye with 2.60 ml of the dye (0.26 mg).

From the values obtained, the averages taken from Table I, and the calibration curve, a calculation was made of the percentage of active principle in the original dyes and those derived from them. The results are given in Table III.

Conclusions

The commercial reagents are impure since, in two that were tested, contents of 31% and 60% of the dye were found, and the impurities are not sensitive to beryllium.

In the spectrophotometric determination of this element, the optical density of the complex formed is a function of the concentration of the dye, even when the latter is found in the maximum quantity compatible with the experimental conditions.

Pure dye can be obtained from the "soluble in sodium hydroxide" fraction of these reagents by crystallization from methyl alcohol following adsorption of some impurities with activated alumina.

Chromatography on alumina and spectrophotometry of the complex formed with beryllium can be used as criteria of purity.

PART II: SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM

Operating conditions for the colorimetric method have been studied by Stross and Osborn,[28] but some variables were not definitely fixed.

The reagent concentration recommended by these authors is 6 ml of a solution with 0.025% total coloring matter in a final volume of 25 ml. This does not accurately define the concentration, however, since this relates to unpurified reagent, with a very variable degree of purity, as was shown in the first part of this publication.

These authors also studied the effect of the pH. We have adopted the buffer system they recommend, but we have changed the sodium hydroxide concentration, and chosen such a buffer concentration that the final solution is 0.180*N* in sodium hydroxide and 0.128*M* in boric acid.

The work of Stross and Osborn was done with a photocolorimeter, and hence the wavelength was not perfectly defined, although the absorption maximum of the filters used is at 525 mμ. Sandell[23] recommends 525 mμ and Vinci[25] 515 mμ. We have not found spectrophotometric curves in the literature which justify this choice; but upon studying the various variables, we established the optimum wavelength as 535 mμ.

The complex formed is highly dissociated, and hence, in our study of the concentration of coloring matter we have expressed the results as functions of the coloring-matter/beryllium ratios, so that they might be generalized to apply to other operating conditions. In this, we took as our reference point the beryllium concentration that yielded an optical density under the adopted conditions that was located approximately in the central portion of the region of least reading error for the spectrophotometer (in our case, 9 γ in 25 ml). This enabled us to establish a coloring-matter concentration such that the coloring-matter/beryllium molar ratio in the final solution is 5:1 for the given beryllium concentration. This makes it possible to obtain a calibration curve that satisfies Beer's law for all the beryllium concentrations that give optical densities in the optimum reading zone of the apparatus.

The sensitivity of the method and the reproducibility of the results were determined under the operating conditions adopted and it was applied to air samples.

It was found that the color developed is due to formation of a highly dissociated complex, in which the coloring-matter/beryllium molar ratio is 1:1.

Experimental Part

Apparatus and Reagents

Spectrophotometer: all the spectrophotometric determinations were performed with a Unicam S.P. 500 spectrophotometer.

p-nitrobenzene-azo-orcinol was obtained by purification of the Hopkins and Williams coloring matter, the "organic reagent for metals," in accordance with the crystallization technique given in Part I.

Standard beryllium solution: (1.000 mg of beryllium per ml) this was prepared in a similar manner to that indicated for the standard solutions used in Part I. All the other solutions used in the work were obtained by appropriate dilutions of this solution.

2*N* sodium hydroxide solution: prepared by dilution of a 50% solution of sodium hydroxide, free from carbonates. Titrated against 1*N* hydrochloric acid prepared from the azeotropic acid. The strength was adjusted to 2.00*N*.

0.64*M* boric acid solution: prepared by dissolving analytically pure boric acid in distilled water. Concentration checked by titration with sodium hydroxide, according to the standard technique.

Calcium chloride solution: (1.00 mg of calcium per ml) prepared by dissolving analytically pure calcium chloride in distilled water. The calcium in an aliquot part was determined gravimetrically by precipitation as the oxalate. The solution was diluted to a concentration of 1.00 mg of calcium per ml.

Magnesium chloride solution (1.00 mg of magnesium per ml): prepared by dissolving analytically pure $MgCl_2 \cdot 6H_2O$ in distilled water. The magnesium in an aliquot part was determined gravimetrically as magnesium pyrophosphate.

Aluminum chloride solution (1.00 mg of aluminum per ml): prepared by dissolving pure metallic

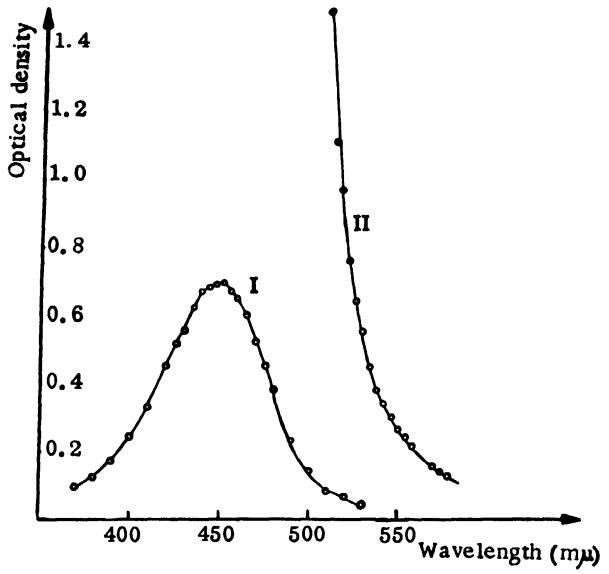

Figure 7a. Spectrophotometric curves. Blank vs water: (I) 0.1 mg of coloring matter; (II) 0.5 mg of coloring matter

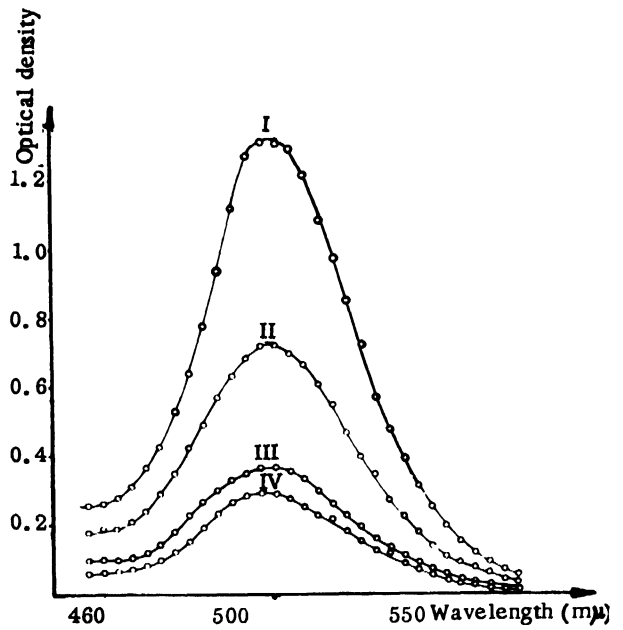

Figure 7b. Spectrophotometric curves. Beryllium complex vs blank: (I) coloring-matter/beryllium molar ratio = 0.5/1; (II) coloring-matter/beryllium molar ratio = 1/1; (III) coloring-matter/beryllium molar ratio = 2/1; (IV) coloring-matter/beryllium molar ratio = 3/1

aluminum in dilute hydrochloric acid and subsequently diluting with distilled water.

Ferric chloride solution (1.00 mg of iron per ml): a standard solution of Mohr salt was prepared, and the iron in an aliquot part was precipitated as the hydroxide after oxidation. The hydroxide was dissolved with dilute hydrochloric acid, and the solution obtained was diluted to 1 mg of iron per ml.

Notes: in all the determinations, the reagents were added in the same order as that indicated in Part I.

The sodium hydroxide indicated includes the amount added with the solution of the coloring matter except where the contrary is stated.

All the solutions of coloring matter were prepared by dissolving in 0.1*N* sodium hydroxide; they were kept in amber-glass bottles and discarded 15 days after being prepared, since the beryllium-sensitivity method indicated that they grew stale. The optical density obtained with 1.00 mg of beryllium and 0.300 mg of coloring matter, in 1-cm cells and at 514 mμ was (1) 0.69; (2) 0.68; (3) 0.68; (4) 0.66; (5) 0.63 in solutions (1) freshly prepared; (2) 10-days old; (3) 15-days old; (4) 20-days old; and (5) 30-days old, respectively.

The amounts of beryllium and coloring matter used are expressed in γ and mg, respectively, without specifying the volume and concentration of the solutions in which they are added, since these varied in the course of the experiments, so as to be able to measure amounts with errors of 1% maximum.

Since the purpose was to determine the smallest possible amount of beryllium per sample, with a view to subsequent employment of the method in analysis of air, the final volume of the system was set at 25.0 and the readings were made in 4-cm cells. Once the variables of the method had been determined, the volume to which the reagent was to be added was therefore set at 5 ml, since this is the largest volume that could be measured with a graduated pipette, compatible with the total volume of 25 ml.

The cells used throughout the work were 4-cm cells unless the contrary is stated.

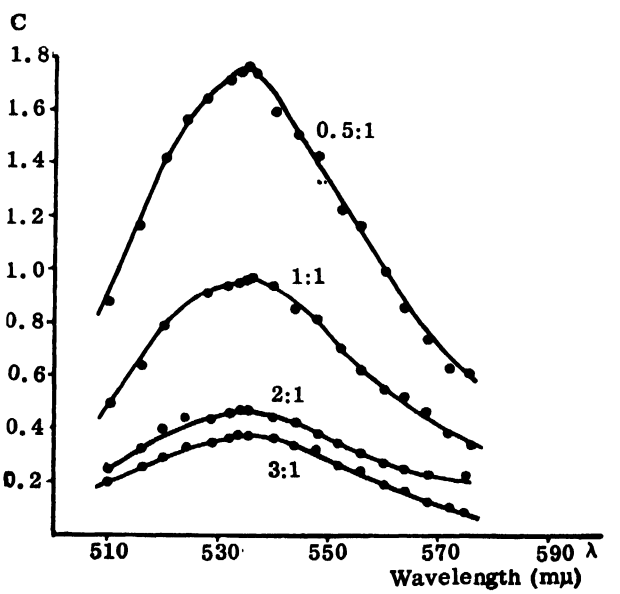

Figure 8. Influence of error in measuring coloring matter as function of the wavelength, for various coloring-matter/beryllium molar ratios. C = ratio of the optical density of the complex vs the blank to the optical density of the blank vs distilled water

Spectrophotometric Curves

Spectrophotometric Curves of the Blanks

Two solutions with a final volume of 25.0 ml were prepared, containing 2.80 ml of 2*N* sodium hydroxide solution, 5.0 ml of 0.64*M* boric acid and 0.100 and 0.50 mg, respectively, of coloring matter. Their optical density relative to distilled water was determined at various wavelengths, using 1-cm cells in the first case. The results are shown in Fig. *7a*.

Spectrophotometric Curves of the Beryllium Complex

Four solutions with a final volume of 25.0 ml were prepared, containing 2.80 ml of 2*N* sodium hydroxide solution, 5.0 ml of 0.64*M* boric acid, 0.50 mg of coloring matter, and 35 γ, 16.5 γ, and 5.5 γ beryllium, respectively. The coloring-matter/beryllium molar ratio in these solutions was 0.5:1, 1:1, 2:1, and 3:1, respectively, for a coloring-matter molecular weight of 273.

The optical density of the above solutions was determined relative to a blank identical with them, except for having no beryllium, for various wavelengths. The results are shown in Fig. *7b*.

Influence of Error in Measuring Coloring Matter as Function of Wavelength

It will be seen from Fig. 7 that the wavelength of maximum sensitivity is 510 mμ. The optical density of the blanks at this wavelength is very high, one of the major errors of the method being that arising from possible differences in the concentration of coloring matter in the solution with beryllium and in the blank. For a given difference in concentrations, the more the optical density of the blank increases and the optical density of the complex with beryllium decreases, the greater will be the resulting error in readings.

The ratio of the optical density of the beryllium complex to that of the blank will be a maximum at the wavelength of least error as determined by the coloring matter.

This wavelength is fixed at 535 mμ for the curve of Fig. 8, traced on the basis of the quotients of the values of the optical density of Fig. *7b* (Curves I, II, III, IV) and of Fig. *7a* (Curve II).

Coloring-Matter Concentration

A series of solutions was prepared with final volume of 25.0 ml, containing 2.80 ml of 2*N* sodium hydroxide, 5.0 ml of 0.64*M* boric acid, 2.0 ml of beryllium, and varying amounts of coloring matter. Blanks were prepared, identical with the previous solutions, but without beryllium.

The optical density of the blanks was determined with respect to distilled water; and that of the beryllium solutions was determined with respect to the blanks at 510 mμ and 535 mμ.

The results are shown in Fig. 9.

If we take 0.5% as the maximum allowable difference between the concentration of coloring matter in the solution containing beryllium and in the blank (a difference caused by errors in measuring the coloring matter and in the final levelling), the error in reading due to this cause is 1% at 535 mμ for a coloring-matter/beryllium molar ratio of 5:1, and 2% at 510 mμ for a 2.25:1 molar ratio. Under these conditions, the sensitivity of the method is equal in the two cases. The slit width is 0.07 and 0.16 mm, respectively.

The foregoing enables us to say that the 535-mμ wavelength is better than the 510-mμ one. The maximum amount of coloring matter to use at this wavelength is greater than at 510 mμ, which makes it possible to predict fulfillment of Beer's law over a wider range of the calibration curve. Despite the higher coloring-matter concentration for equal sensitivity conditions for the apparatus, the slit is cut down by half.

The following experiment was performed to verify the fulfillment of Beer's law under the above conditions:

Two series of five solutions each were prepared. With a final volume of 25.0 ml the solutions of each series contained 2.80 ml of 2*N* sodium hydroxide, 5.0 ml of 0.64*M* boric acid, and varying amounts of beryllium. The two series had 1.365 and 0.613

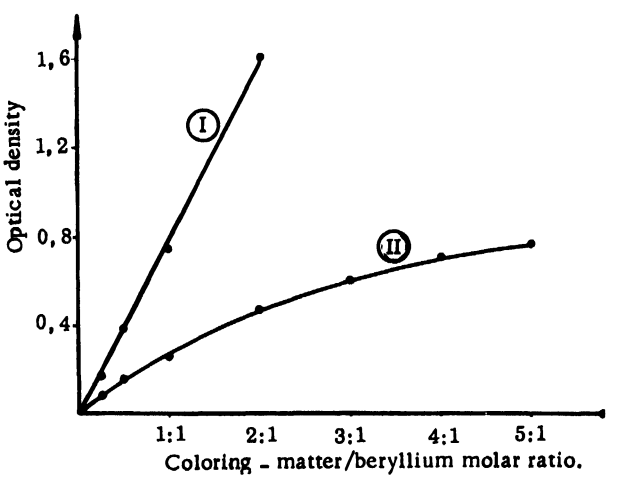

Figure 9a. (I) Blank vs distilled water; (II) 9 γ of beryllium vs blank. Readings at 510 mμ

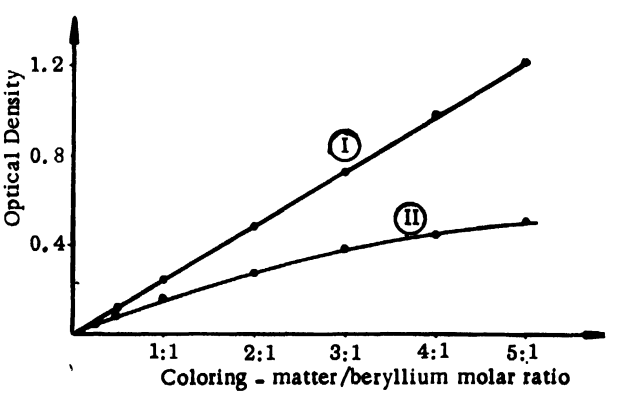

Figure 9b. (I) Blank vs distilled water; (II) 9 γ of beryllium vs blank. Readings at 535 mμ

mg of coloring-matter, respectively (coloring-matter/beryllium molar ratios of 5:1 and 2.25:1, respectively, for 9γ of beryllium).

The optical density was determined with respect to blanks identical with the solutions but containing no beryllium, at 535 mμ for the first series and 510 mμ for the second.

The results are given in Fig. 10. It is seen that, in point of fact, Beer's law applies over a larger region of the calibration curve at 535 mμ and with a 5:1 coloring-matter/beryllium molar ratio.

Effect of the pH

Effect of the Sodium Hydroxide Concentration

A series of solutions was prepared, with final volume 25.0 ml, containing 5.0 ml of 0.64*M* boric acid, 1.365 mg of coloring matter, 9.0 γ of beryllium, and varying quantities of 2*N* hydroxide solution. Blanks were prepared identical with the above solutions, but without beryllium.

At 535 mμ the optical density of the blanks was determined with reference to distilled water, and that of the solutions containing beryllium with reference to the corresponding blanks. The results are shown in Fig. 11*a*. The ml of sodium hydroxide indicated in this figure do not include the amounts added with the reagent (5 ml of 0.1*N* sodium hydroxide).

Effect of the Boric Acid Concentration

A series of solutions was prepared, with final volume 25.0 ml, containing 2.80 ml of 2*N* sodium hydroxide, 1.365 mg of coloring matter, 9.0 γ of beryllium, and varying amounts of 0.64*M* boric acid solution. Blanks were prepared identical with the above solutions, but without beryllium.

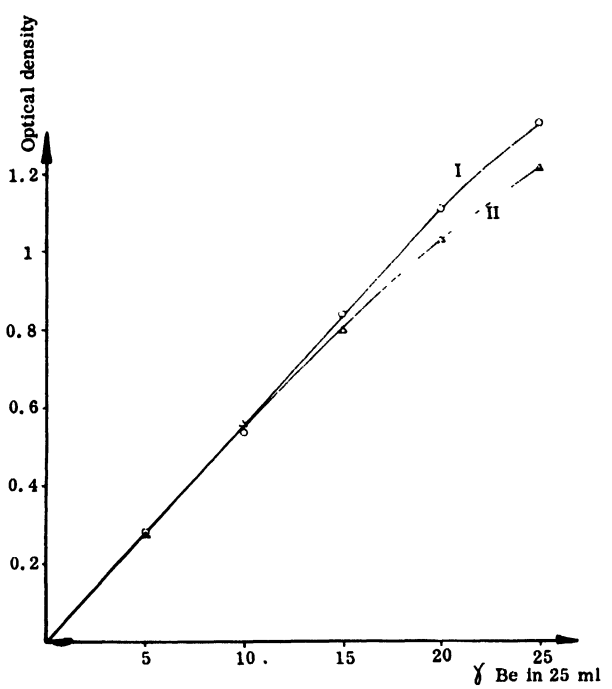

Figure 10. Influence of operating conditions on compliance with Beer's law. (I) 1.365 mg of coloring matter in 25 ml (Coloring-matter/beryllium molar ratio = 5/1 for 9 γ of beryllium). λ = 535 mμ. (II) 0.613 mg of coloring matter in 25 ml. (Coloring-matter/beryllium molar ratio = 2.25/1 for 9 γ of beryllium) λ = 510 mμ

At 535 mμ the optical density of the blanks was determined with reference to distilled water, and that of the solutions containing beryllium with reference to the corresponding blanks. The results are shown in Fig. 11*b*.

Figure 11 indicates that the pH has a marked effect on the color of the blanks and of the solutions with beryllium. Using 5.0 ml of 0.64*M* boric acid, sensitivity is found to be a maximum between 1.6 and 1.75 ml of sodium hydroxide (pH about 11.5). It is advisable, however, to get some distance away from the region where the curve of the beryllium complex exhibits a sharp drop; for this reason, we adopted 2.00 ml of 2*N* sodium hydroxide as the amount to be used not including the sodium hydroxide added with solution of coloring matter, equivalent to 0.25 ml of 2*N* solution.

It will be seen from the curves that measurements of the sodium hydroxide and boric acid solutions should be made to within 1% and 2%, respectively, in order to avoid errors of over 1% in the determination.

Effect of Time

A solution was prepared with a final volume of 25.0 ml, containing 2.25 ml of 2*N* sodium hydroxide, 9.0 γ of beryllium, 5.0 ml of 0.64*M* boric acid solution, and 1.365 mg of coloring matter. A blank of identical composition, except for the absence of beryllium, was also prepared.

The optical density of the solution at 535 mμ was determined with reference to the blank at one hour intervals after the time of its preparation.

The values obtained are given in Table IV.

The table shows that the influence of the time elapsing between preparation of the solution and taking the reading is small; the decrease is of the order of 1% in two hours.

Sensitivity of the Method and Reproducibility of the Results

A calibration curve was plotted under the adopted working conditions; this curve is given in Fig. 12. The determinations were made with reference to independently prepared blanks.

The sensitivity of the method, calculated in conformity with this curve, is 0.0025 γ per cm^2 for an optical density of 0.001.

Ten solutions were prepared with 25.0 ml final volume, containing 2.25 ml of sodium hydroxide, 7.0 γ of beryllium, 5.0 ml of 0.64*M* boric acid and 1.365 mg of coloring matter, in order to establish reproducibility of the results. The optical density at 535 mμ was determined with reference to independently prepared blanks. The results are given in Table V.

According to these results, the precision of the method is 3% for the mean of two determinations in the optimum zone of the spectrophotometer, cal-

Table IV. Effect of Time

Time, hours	*Optical density*
0	0.578
1	0.575
2	0.572
3	0.570
4	0.570

culated on the basis of 9 degrees of freedom, and the reliability limit may be set as 95%.

Coloring-Matter Beryllium Molar Ratio in the Resulting Complex

Job's methods of continuous variation was employed to determine this.[9,11,13] A series of solutions was prepared having 25.0 ml final volume, containing 5.0 ml of 0.64*M* boric acid, 2.25 ml of 2*N* sodium hydroxide, and such amounts of coloring matter and beryllium that the molar sum was constant and equal to 1.6×10^{-4} in each solution, and the molar fraction $Be/M_{col} + M_{Be}$ was varied between 0.1 and 0.9.

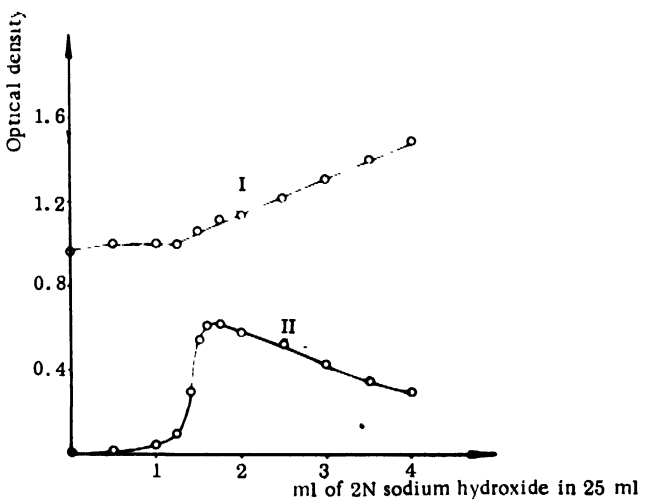

Figure 11a. (I) Blank vs distilled water; (II) Beryllium complex vs blank

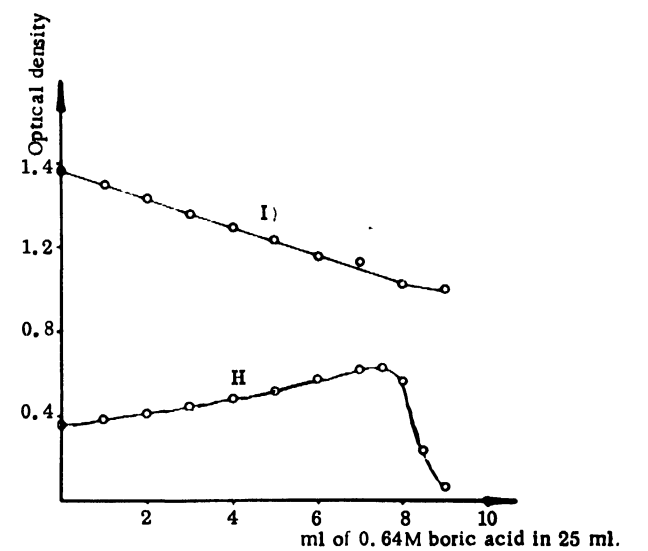

Figure 11b. (I) Blank vs distilled water; (II) Beryllium complex vs blank

Table V. Reproducibility of the Results

Solution	*Optical density*
1	0.431
2	0.440
3	0.454
4	0.445
5	0.441
6	0.444
7	0.443
8	0.441
9	0.430
10	0.445

A series of blanks was prepared, identical with the above solutions except that they contained no beryllium. The spectrophotometric curves corresponding to different coloring-matter/beryllium molar ratios are shown—Fig. 13. The readings at 500 mμ were taken in 1 cm cells in order to avoid very wide slits, but the results obtained were multiplied by four for greater clarity in the figure.

The experiments indicated that the color produced is due to the formation of a single, highly dissociated complex, in which the coloring-matter/beryllium molar ratio is 1:1.

Application to Analysis of Air Samples

Type SS 589[1] filter paper[20,21] was used in taking the air sample. The wet method was used for destroying the organic matter before analysis, in order to prevent the beryllium losses that occur during calcination.[21] Under these conditions, the final solution is highly acidic and unsuited for the colorimetric determination of beryllium, so that a carrier must be used to recover this element.

Aluminum was used for this purpose; and we primarily investigated the recovery of beryllium during the destruction of the organic matter and concentration with the carrier.

A series of six precipitating beakers was prepared. An SS 589[1] filter paper 11 cm in diameter was placed in each jar, and 0.60 ml, 1.20 ml, 1.80 ml, 1.40 ml and 3.00 ml, respectively, of a solution of beryllium sulfate (5 γ of beryllium/ml) was added. We added 4 ml of sulfuric acid (sg = 1.84) and 8 ml of concentrated nitric acid to each jar, allowing each acid to act for 10 minutes and then heating gently, with the jar covered, until the nitrous fumes were eliminated. Destruction of the organic matter was completed by adding 3 drops of concentrated perchloric acid and heating until white fumes were given off. The silica was eliminated in a platinum evaporating dish with 3 drops of 48% hydrofluoric acid.

This technique yielded completely colorless solutions in less than 3 hours. They were transferred to 10-ml centrifuge tubes containing 1 ml of aluminum chloride solution (1 mg aluminum per ml) and 1 ml of ammonium chloride solution (200 mg of ammonium chloride per ml) each. The final volume

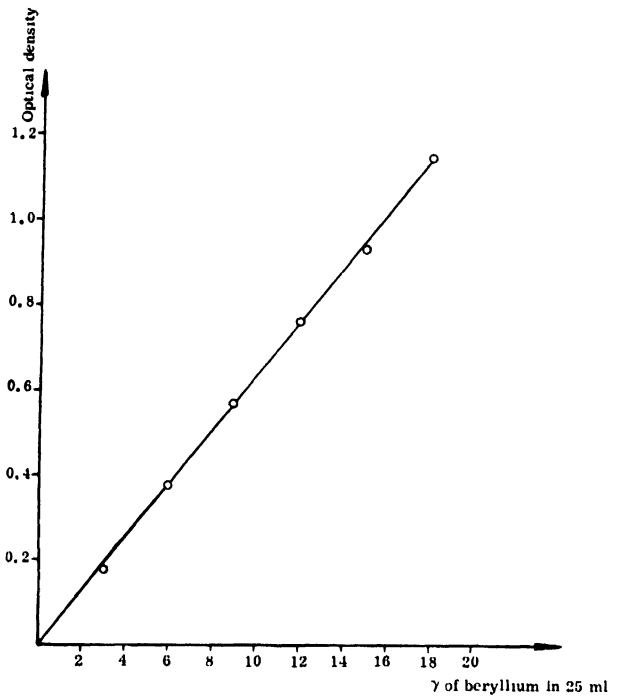

Figure 12. Calibration curve for the conditions adopted

was adjusted to 8 ml, and the solution was neutralized by adding ammonium hydroxide dropwise.

The precipitate obtained was centrifuged, washed with 5 ml of distilled water, centrifuged again, dissolved in 2.02 ml of *2N* sodium hydroxide, and transferred to a 25.0-ml flask.

After washing the tube with 5 ml of distilled water, the color was brought out under the conditions we have adopted, and read against blanks prepared in the usual way.

The results are summed up in Table VI.

2.40 ml and 3.00 ml, respectively, of a solution of beryllium sulfate (5 γ of beryllium/ml) was added. to 10–ml centrifuge tubes containing 1 ml of alumi- transferred to a 25.0–ml flask.

It follows from the above table that recovery is 97% ± 3% between 3 and 15 γ, calculated on the basis of 4 degrees of freedom, for a reliability limit of 95%.

Table VI. Recovery of Beryllium

γ of beryllium added	*Optical density*	*γ of beryllium found*
3.0	0.175	2.8
6.0	0.355	5.6
9.0	0.558	8.9
12.0	0.740	11.8
15.0	0.908	14.4

Iron, calcium and magnesium were selected for study of the interferences,[35] since these are the elements among those normally found in air samples that are most likely to affect beryllium determination.

Silica was left out of consideration, since it is eliminated in the preliminary preparation of the sample.

Ten samples of air each of 10 cubic meters, were analyzed spectrographically in order to determine the approximate concentration of the elements under consideration. It was found that they contained 100 γ of calcium, 50 γ of magnesium and 100 γ of iron on the average.

A series of 11 centrifuge tubes was prepared, numbered from 1 to 11, each containing, 1.40 ml of beryllium sulfate solution (5 γ of beryllium/ml) in a final volume of 8 ml. Seven of these tubes (Nos. 1, 2, 3, 6, 7, 10, and 11) contained, in addition, 1 ml of aluminum chloride solution (1 mg of aluminum per ml), 1 ml of ammonium chloride solution (200 mg of ammonium chloride per ml), and varying amounts of iron, calcium, and magnesium, respectively. Varying amounts of calcium and magnesium were added to the remaining four.

The tubes containing the carrier were precipitated, centrifuged, etc., following the same technique employed in the recovery experiment. *2N* sodium hydroxide was added to the other tubes (2.00 ml to Nos. 4 and 8, and 2.02 ml to Nos. 5 and 9). All the solutions were transferred to 25-ml flasks with the precautions referred to above, and the color was developed in each flask under the conditions we have adopted. The optical density was read as against blanks prepared in the usual manner.

The values obtained are summed up in Table VII.

Table VII. Interferences

Tube no.	*Interference studied*	*Amt. of added interf., mg*	*Aluminum carrier, mg*	*Beryllium added, γ*	*Optical density*	*Beryllium found, γ*
1	Fe	0.050	1	7.0	0.440	7.0
2	Fe	0.200	1	7.0	0.431	6.9
3	Fe	0.050	1	7.0	0.420	6.7
4	Mg	0.100	–	7.0	0.380	6.1
5	Mg	1.00	–	7.0	0.170	2.8
6	Mg	1.00	1	7.0	0.430	6.9
7	Mg	1.00	1	7.0	0.440	7.0
8	Ca	0.100	–	7.0	0.450	7.1
9	Ca	1.00	–	7.0	0.430	6.9
10	Ca	1.00	1	7.0	0.440	7.0
11	Ca	1.00	1	7.0	0.450	7.1

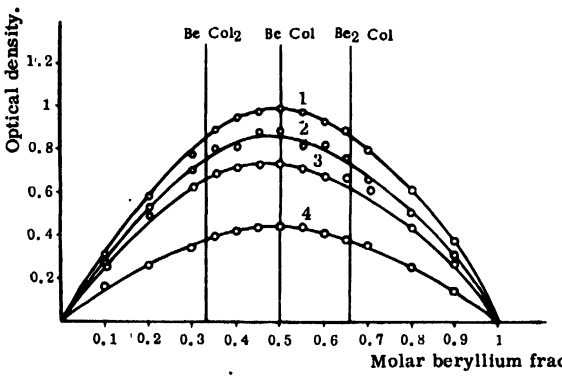

Figure 13. Coloring-matter/beryllium molar ratio in the complex. Wave lengths: (1) 510 mμ, (2) 500 mμ, (3) 525 mμ, (4) 540 mμ

It follows from Table VII that iron does not interfere to any great extent up to 1 mg per sample, when the carrier (1 mg of aluminum) is present.

Magnesium interferes seriously when no carrier is used, even in amounts of the order of 100 γ per sample, but 1 mg of this element does not interfere when a carrier is used.

Calcium produces no interference in any case.

CONCLUSIONS

Beryllium reacts with *p*-nitrobenzene-azo-orcinol; over a specific pH range a single red highly dissociated complex is produced in which the Be/coloring-matter molar ratio is 1:1.

The reaction makes it possible to determine beryllium spectrophotometrically if strict control of the operational conditions is exercised.

The final solution should be 0.180*N* in sodium hydroxide and 0.128*M* in boric acid. The coloring-matter concentration in this solution should be such that the coloring-matter/beryllium molar ratio is about 5:1, compared with the beryllium concentration in the middle portion of the range of beryllium concentrations to be determined. The spectrophotometric reading should be taken at 535 mμ.

Under these conditions, if the volume of the final solution is 25.0 ml, and the length of the cells used is 4 cm, the range of beryllium concentrations that can be measured within the spectrophotometer's optimum reading zone is 3 to 16 γ, Beer's law being satisfied over this region. The sensitivity is 0.0025 γ per cm^2 for an optical density of 0.001.

The precision of the method for the mean of two determinations in the spectrophotometer's optimum reading zone operating with pure beryllium solutions, is calculated from the data of Table 5 (9 degrees of freedom). Setting the limit of reliability at 95%, this proves to be ± 3%.

The method can be applied satisfactorily to determination of beryllium in air samples. Recovery may be estimated at 97 ± 3% between 3 and 15 γ calculated on the basis of four degrees of freedom (Table VI) for a reliability limit of 95%.

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Spectrophotometric Evaluation of Microquantities of Boron

By Julia F. Possidoni de Albinati and Rafael H. Rodríguez Pasqués,* Argentina

The process which is the subject matter of this article is based on the known formation of a compound of deep red color when boric acid is mixed with curcumin (yellow dye extracted from the turmeric root) in an acid medium. Schulumberger first used this reaction for qualitative analysis around 1866, and then Cassal and Gerrans added oxalic acid in 1903 to intensify the color obtained. Since then the method has been studied repeatedly and extended to quantitative analysis.[1]

Russell published, in 1944, a revision of the literature written up to that date.[2]

Recently a number of workers have studied the application of the absortiometric technique, and perhaps the best work published on the subject is Naftel's;[3-7] all stress the extraordinary sensitivity of the reaction, without insisting on the practical difficulties.

Until recently, all we knew about the nature of the reaction were surmises, and it was even believed that the red color was that of a boron free curcumin polymer. Spicer and Strickland published in 1952, three interesting articles[8,9,10] on the mechanism of the reaction, in the presence and in the absence of oxalic acid and arrived at the conclusion that the yellow dye forms, in both instances, complex combinations with the boric acid, which they named *rosocyanin* and *rubro-curcumin.*

In the former, the boron/curcumin molar ratio is 1:2; and the latter contains oxalic acid in its molecule, so that the boron/curcumin/oxalic ratio is 2:2:2. Since molar extinction is about the same in both complexes, rosocyanin formation is theoretically twice as sensitive as that of rubro-curcumin; however, it is preferable in actual practice to obtain the latter because it gives a higher yield and consequently, more intense colors. According to the authors mentioned, the reaction may be written as follows:

$$2H_3BO_3 + 2\begin{matrix}COOH\\|\\COOH\end{matrix} + \underset{\text{curcumin}}{2C_{21}H_{20}O_6} \rightleftarrows 6H_2O + \underset{\text{rubro-curcumin}}{C_{46}H_{38}O_{20}B_2}$$

The boron in the sample should be changed to boric acid, which is readily separated by distilling it as its methyl ester and recovering in a dilute solution of sodium hydroxide; evaporating the distillate to dryness, finally extracting the boron as sodium borate, together with the surplus alkali.

In order to carry out the reaction, neutralize the alkali, add the "turmeric reagent", and dehydrate by heating to a moderate temperature. The rubro-curcumin thus formed is dissolved in methanol or acetone, and the intensity of the red color is compared spectrophotometrically with known samples, prepared in a similar fashion. Separation by distillation insures the absence of interferences, and is easily made. However, the formation conditions of the colored complex are somewhat critical, and special care should be taken in order to have consistent results. The sensitivity of the method is very great.

TECHNIQUE

General

The determination of traces of boron requires special refinements of the technique, in order to avoid any contamination from the outside. For this reason, boron free materials and previously purified reagents should be used. This precludes the use of borosilicate glass containers.

Before use, the distilling equipment and all the glass, quartz and platinum equipment is cleaned and decontaminated from boron, washing successively with a sulphuric-chromic acid mixture, water, redistilled water and boiling methanol. Boiling of the methanol should be continued for several minutes inside the containers to be decontaminated.

Reagents and Equipment

Redistilled water: Obtained from quartz still. Keep in a polyethylene container.

Boric acid standard solution: One gamma per ml, prepared with boric acid and redistilled water. Keep in a polyethylene container.

Concentrated perchloric acid: Boron is eliminated by several hydrofluoric acid evaporations in a platinum crucible. Keep in a quartz or boron-free glass vial.

Methanol, boron free: Leave for two days in contact with lime treated with sodium, distill, recover the middle fraction, and redistill after another period of two days of contact with lime. Keep in polyethylene bottle.

Original language: Spanish.

* Comisión Nacional de la Energía Atómica.

Ethanol, boron free: Prepare, as explained for the methanol.

Sodium hydroxide, 10% solution: Prepare with pure chemical, previously examined to ensure that it is *sufficiently* boron free.

Oxalic acid, boron free: Recrystallize twice, in redistilled water. Keep in polyethylene bottle.

Hydrochloric acid, concentrated: Analyze each lot.

Hydrochloric acid 1 + 4: Prepared by dilution of above with redistilled water.

Curcumin: British Drug Houses chemical was used, crystallized, for laboratory use.

Curcumin reagent: Dissolve 15 gm oxalic acid in ethanol, add 15 ml concentrated hydrochloric acid and 85 ml redistilled water. Add 1 gm curcumin and make up to one liter with ethanol. Filter, and keep in a polyethylene bottle.

Distillation apparatus: Quartz, to separate boron as methyl borate. Flask capacity approximately 200 ml (Fig. 1).

Precipitation vessels: Quartz or boron free glass, about 100 ml capacity.

Platinum evaporating dishes: 45 ml capacity, of same thickness and cross section.

Thermostatic bath: Plus stirrer for same.

Spectrophotometer: "Unicam" model SP 500 or equivalent; 10 and 20 mm light cells.

Processing of Uranium Samples and Compounds

Use an amount containing 0.1 to 5 γ of boron. Dissolve in suitable manner, bearing in mind the volatility of boric acid in steam in order to avoid loss. Pass to distillation beaker, make alkaline to methyl red, and proceed as described below.

Treatment of Graphite Samples

Grind in an agate mortar after decontamination from boron. Take a sample of suitable size, transfer to a platinum crucible, add hot saturated barium hydroxide solution and homogenize the paste using a platinum wire.

Insert the crucible in a cylindrical quartz oven and gradually heat in a slow oxygen flow to 750–800°C, until complete combustion of the graphite.[12] The gas ejected is bubbled through an alkali solution.

Transfer the alkali residue from the crucible and the alkaline solution to the distillation flask (Fig. 1).

Separation of Boron by Distillation

Heat the alkaline sample contained in the flask, Fig. 1, and boil off almost all the water present.

Cool. Add, by means of the separation funnel, enough concentrated perchloric acid to acidify the system, and add 30–50 ml methyl alcohol. Place the flask in boiling water and collect the methanol and methyl borate formed (B.Pt. 68°C) in a quartz precipitation vessel in which the tip of a refrigerating tube is dipped into an adequate amount of a solution made with 0.2 ml 10% sodium hydroxide, and enough redistilled water to cover the outlet tip. There is no danger of explosion due to overheating, since the operation is performed in a double boiler.

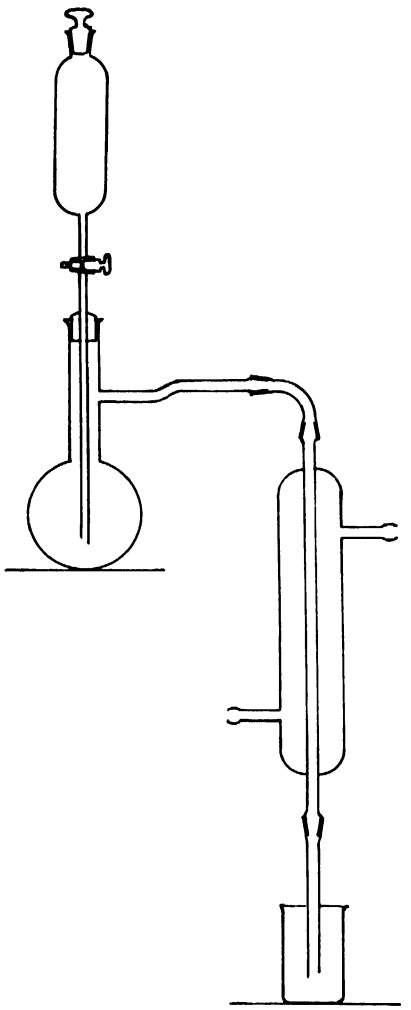

Figure 1

As the contents of the flask become nearly dry, add a new portion of methyl alcohol, and repeat the distillation three times, collecting always in the same vessel.

As the distillate is being recovered, some turbidity or white precipitate may appear in it, due to the carbonation of the hydroxide, but this will be no hindrance whatsoever.

Concentrate the alkaline aqueous and alcoholic solution in a double boiler to a few milliliters, and transfer quantitatively to a platinum evaporation dish.

Obtain, in a similar way, a "distilled blank", the purpose of which will be to subtract from the boron found in the sample, that which was present in the reagents; it may be omitted when the latter are completely boron free.

Development of the Colored Complex

Prepare in their own platinum dishes, a boron free blank and the necessary standard samples, with 0.2 ml of 10% sodium hydroxide, and the corresponding volumes of a standard boric acid solution. Heat all prepared dishes in a double boiler or sand bath at moderate temperatures, until the contents are

totally dry: the final stage of this dehydration process should be watched very carefully since losses may occur due to the sputtering produced by the cracking of the crystalline residue.

Cool, add to each dish the exact volume of 1 + 4 hydrochloric acid needed to acidify the contents stirring carefully with a platinum wire. It is very important that the volume of acid added to all the capsules be the same (about 0.3 ml).

Next, add 5 ml of "curcumin reagent" to each dish, and simultaneously place them in a bath, the temperature of which is stabilized between 55 and 58°C, enclosed in a fume-cupboard, where they are kept until total dehydration. This is the most critical stage of the process; it is absolutely necessary that the evaporations be carried out simultaneously, and non-compliance with these condition will give inconsistent results.

The colors will be deeper if the drying time is short. Platinum dishes are convenient for this very reason, due to the high thermal conductivity of this metal.

Spectrophotometric Measurement

Cool the dishes; add 15 or 20 ml methanol (or acetone), measuring exactly, stirring with platinum wire to dissolve the dye. The volume may be increased if the colors are excessively deep.

Filter the colored alcoholic solutions (yellow, orange, red) through fast dry filter paper, in order to separate the saline residue, and fill the absorption cells (10 or 20 mm) with the clean filtrates.

As previously stated, the color intensities depend on the temperature and duration of evaporation; for this reason, it is impossible to draw a permanent calibration curve but, since Beer's law is strictly observed, the blank and one single standard should suffice to establish it for each operation; in practice. It is also convenient to use a second standard sample, in order to check the required compliance with the linear law.

The extinction readings are taken at 540 mμ. The intense yellow color of the blank does not interfere since, at that wavelength, corresponding to maximum absorption of the rubro-curcumin, curcumin itself does not absorb appreciably.

The corresponding extinctions are calculated from the transmittance values and a straight line is drawn as a function of the boron concentrations. The boron content of the sample is determined by the position of its optical density or extinction along the line.

EXPERIMENTAL PART

Recovery of Boron by Distillation

The quantitive recovery of boric acid by formation of the methyl ester and distillation of same has very clearly been proved. Sandell[11] quotes Landmark to the effect that 0.1 γ are recovered by distillation. Yoe and Grob[13] found in a group of 15 distillation of approximately 7 γ, an average loss no greater than 1.65% (0.12 γ). Our recovery rates also were of the same order. In the following experiments, the blanks and standard are distilled, and subjected to analytical processes together with "direct" samples (not distilled), containing the same amounts of boron. The results may be seen in Table I.

Spectral Absorption of the Complex

Prepare a sample with 2 γ boron and a blank, both containing the same amount of curcumin. Determine their extinctions between 485 and 600 mμ, and, by calculating the differences between them, draw the absorption curve of the complex, which shows a maximum at 540 mμ.

It should be pointed out that the curcumin consumed in the formation of rubro-curcumin represents about 1.3% of the total added, and this was taken into consideration when drawing up Fig. 3, Fig. 2 and Table II.

Compliance with Beer's Law

Figure 3 shows the results of some experiments. It may be observed that the gradients of the lines are substantially different, due to unequal drying times. The samples of straight line 3 had 2 ml sodium hydroxide, as compared with 0.2 ml for the other two.

Influence of Drying Time

This is shown, in Tables III and IV, and Fig. 4. The differences in drying time were obtained by using quartz containers of different cross sections

Table I

Sample no.	*Boron added,* γ	*Boron recovered,* γ	*Difference* γ
1	0	0	— 0
2	0.10	0.14	+ 0.04
3	0.10	0.06	— 0.04
4	0 50	0.46	— 0.04
5	2.00	1 94	— 0.06
6	3.00	2.99	— 0.01
7	3.00	2.99	— 0.01
8	3.00	2.94	— 0.06

Table II

λ mμ	*Curcumin extinction (A) Fig. 1*	1.3% (A) (B)	*Curcumin Complex extinction Surplus (C) Fig. 2*	*Complex extinction (C — A B) =D Fig. 3*
485	0.780	0.010	1.174	0.404
490	0.466	0.006	0.762	0.302
495	0.284	0.004	0.520	0.240
500	0.177	0.002	0.392	0.217
505	0.112	0.001	0.319	0.208
510	0.077	0.001	0.282	0.206
520	0.041	0.001	0.262	0.216
530	0.025	—·—	0.260	0.235
540	0.018	——	0.264	0.246
550	0.013	——	0.252	0.239
560	0.009	—·—	0.215	0.206
570	0.007	——	0.149	0.142
580	0.002	——	0.092	0.090
590	0.002	——	0.054	0.052
600	0.001	—·—	0.018	0.017

for each series, instead of using platinum dishes (Table III), or of surrounding each capsule of the "slow series" with another (Table IV). Evaporations were initiated simultaneously, and the samples were removed as they reached the dry state.

In order to decide whether the important factor was the actual drying time or the total time in the thermostat, the experiment shown on Table V and Fig. 5 was undertaken. Platinum dishes of the same cross section were used. In them, samples were then prepared which had increasing boron contents. All the dishes remained in the thermostat for 65 minutes, and the drying time of each was registered. In the two dishes containing duplicates, drying was slower.

The straight line of the extinction curve shows the consistency of the data obtained with the simultaneously dried dishes.

Sensitivity, Precision

Expressed according to Sandell[11] and estimating on the basis of line 2 of Fig. 3 (slit · 10 mm), the sensitivity obtained is 0.00014 γ/cm^2.

The precision of the method is determined by such critical factors as simultaneity of evaporation and

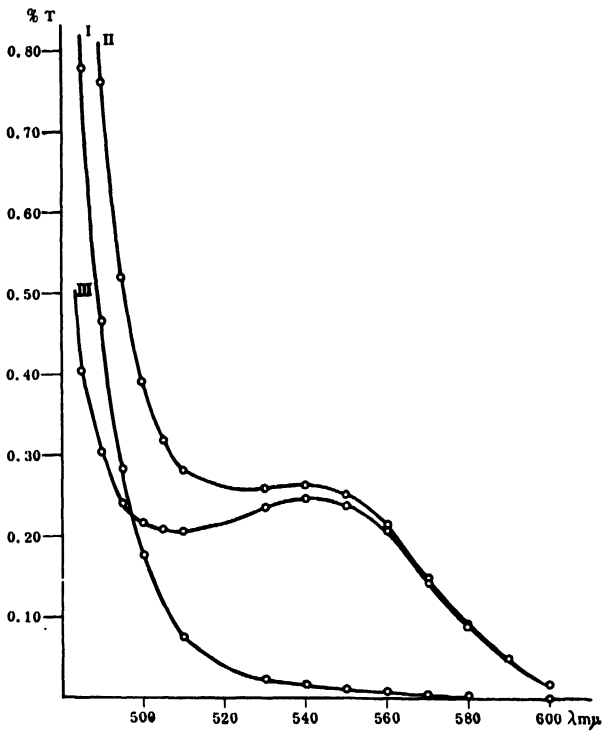

Figure 2

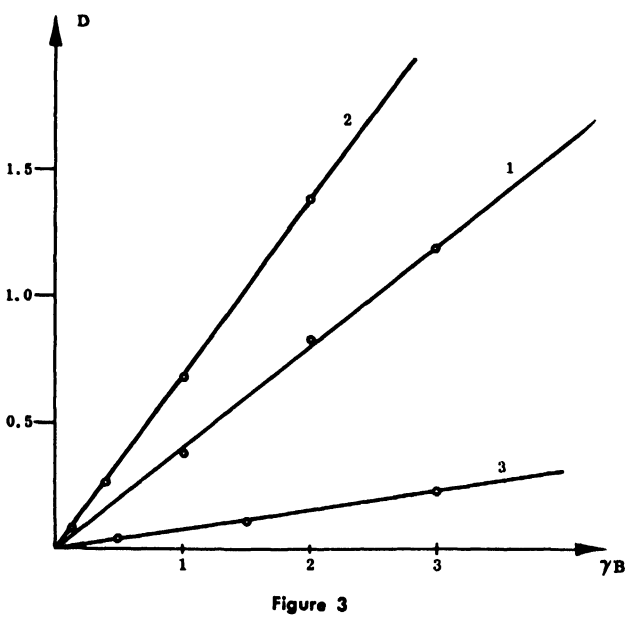

Figure 3

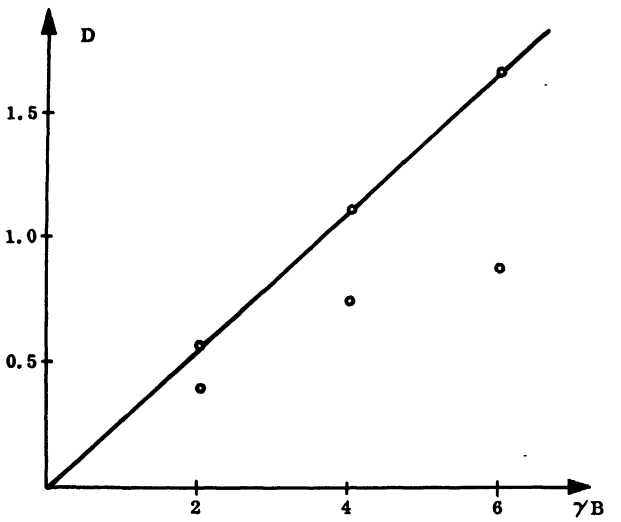

Figure 4

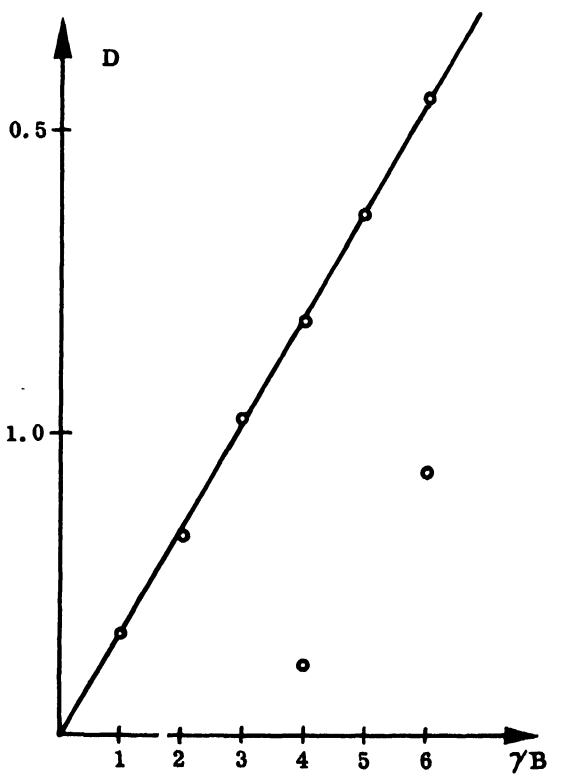

Figure 5

Table III

Series	*A*		*B*		*C*	
Boron, γ	3	3	3	3	3	3
1 + 4 hydrochloric acid	0.2	0.2	0.1	0.1	0.1	0.1
Redistilled water, ml	0.2	0.2	0.3	0.3	0.3	0.3
Curcumin solution, ml	5	5	5	5	5	5
Drying time, min	90	155	70	125	70	120
Extinction difference	0.569		0.589		0.596	

Table IV

Series	*Boron*	*Drying time. min*	*Reading* % *T*	*D*
	0	45	100	0
A	2	45	27.5	0.560
	4	45	7.5	1.125
	6	45	2	1.699
	0	45	100	0
B	2	75	40	0.398
	4	100	18	0.745
	6	110	13	0.866

Table V

Sample no.	*Boron*	*Drying time*	*Transmittance* % *T*	*Extinction D*
1	0	50 min	100.–	0
2	1	50 min	66.	0.180
3	2	50 min	47.5	0.323
4	3	50 min	30	0.523
5	4	50 min	21	0.678
6	4	65 min	77.5	0.111
7	5	50 min	14.5	0.839
8	6	50 min	9	1.046
9	6	60 min	36	0.444

smallness of the losses during distillation. In our experiments we have been able to keep the total error under 0.06.

CONCLUSIONS

The process described is not essentially different from those of other authors mentioned in the references. Our objective was the application of this technique to the estimation of boron in uranium and graphite, to study the variables which had a deciding influence on securing the correct data, and to fix the exact details of the technique which were to be observed.

Special consideration was given to the influence of the drying time in the development of colors, observing the following:

The condition of simultaneous evaporation of the dishes is very critical in this phase of the process, if consistent data are to be obtained.

The color intensity increases as the drying time decreases; therefore, the use of platinum equipment is indicated in order to achieve greater sensitivity.

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Separation and Determination of Zirconium in Samples of Uranium and Beryllium

By J. F. Possidoni de Albinati and J. H. Capaccioli,* Argentina

In a recent article[1] Grimaldi and White mentioned the use of dimethylamino-azo phenylarsonic acid (pararsonic acid) as a selective precipitant for Zr. With this reagent, the authors succeeded in directly separating microquantities of this element and they applied the technique—following precipitation of the hydroxides using iron as a carrier, and prior to colorimetry with quercetin—to the determination of zirconium in silicate. Under the conditions of work described, the specificity of pararsonic acid as regards the separation of zirconium from the remaining elements of Group 4B (except hafnium) is very high, and it has also been mentioned that an efficient separation of many other elements is achieved, among which uranium and beryllium (up to 50 mg of U_3O_8 and BeO).

An attempt was made to extend the application of the separation process to much larger quantities of uranium and beryllium, in order to determine the zirconium content by applying a colorimetric technique with hydroxyanthraquinone.

The colorimetric techniques which use sodium alizarine-sulfonate and quinalizarine were used in this sense. Preference was given to the first product and, accordingly, a study was made of the behavior of the elements which are most frequently encountered in the solution in which zirconium is being estimated, when separated from the samples reviewed in this work.

It should be pointed out that the technique does not provide for discrimination between zirconium and hafnium, so that, with the proposed technique, the results obtained represent the sum of both elements. The chemical separation of zirconium and hafnium is extremely difficult; until recently, resort was had to the tedious fractional crystallization technique of potassium fluozirconiates and fluohafniates, or to the repeated fractionation and precipitation of the corresponding phosphates. Recently, fractionating methods were offered for these elements by ionic interchange on resins;[2] those methods are in full development, they apply to complex cations or anions. A separation based on selective extraction with thenoyltrifluoracetone and other β-diketones also was offered as a means of effecting this separation.

With respect to the hydroxyanthraquinones, one gram of zirconium is spectrophotometrically equivalent to 2.55 grams of hafnium,[4] upon finding the value corresponding to a hundred γ of zirconium, and assuming a ratio of Zr:Hf = 95:5, this value will correspond to the effective presence of 94.3 of zirconium and 5.3 γ of hafnium.

SEPARATION OF ZIRCONIUM

In general outline, the technique of zirconium separation is that used by the authors already mentioned.[1] The sample of uranium or beryllium, as the chloride, is dissolved in 10 ml of hydrochloric acid (1:1), 5 ml of a 0.3% solution of pararsonic acid in hydrochloric acid (1:1) are added, and the volume is adjusted to 50 ml. Small amounts of the oxidizing agents present in the sample will destroy the reagent. In order to avoid this, the solution is treated with hydroxylamine before it is added. It is digested at approximately 100°C during at least an hour, 0.5 gm of paper pulp treated with dilute hydrochloric acid (boiling) are added and then washed with hot water and the solution filtered on a fine pore paper. Washing is carried out hot, with a dilute hydrochloric solution of pararsonic acid.

The paper, with precipitate, is transferred to a platinum crucible, dried and calcined at a temperature of no more than 500°C.

The oxide is dissolved in concentrated sulfuric acid, the excess is removed, the sulfate treated with hydrochloric acid (1:1) in order to dissolve it, and zirconium is determined by colorimetry in the remaining solution.

When the sample contains large quantities of uranium, it is advisable to repeat the precipitations because, in the first, some of the uranium is absorbed in the filter paper and in the pulp, which gives high values in the colorimetric determination with alizarine.

In a series of precipitations of zirconium in samples containing two grams of uranium, the results in Table I were obtained, as shown on the following page.

Table II shows the results obtained by applying the separation technique described to synthetic samples; colorimetric determination was carried out with sodium.

Original language: Spanish.

* Comisión Nacional de la Energía Atómica, Argentina.

SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM

The use of the hydroxyanthraquinones (alizarine, quinalizarine, and purpurines) was described by Liebhafsky and Winslow.[5] Other authors[6] use the relevant sulfone derivatives, which offer the advantage of being soluble in water.

In this work, use was made of the sodium alizarine sulfonate.

The colorimetric technique includes the following steps:

(*a*) Transfer the hydrochloric solution of zirconium to a 25 ml beaker.

(*b*) Add 2.0 ml of the 0.1% solution of sodium alizarine sulfonate.

(*c*) Neutralize with concentrated ammonium hydroxide until the reagent shows a purple color (pH above 5.6).

(*d*) After two minutes (±½ minute) neutralize the excess alkali with hydrochloric acid (1:5), drop by drop, until the alizarine changes color.

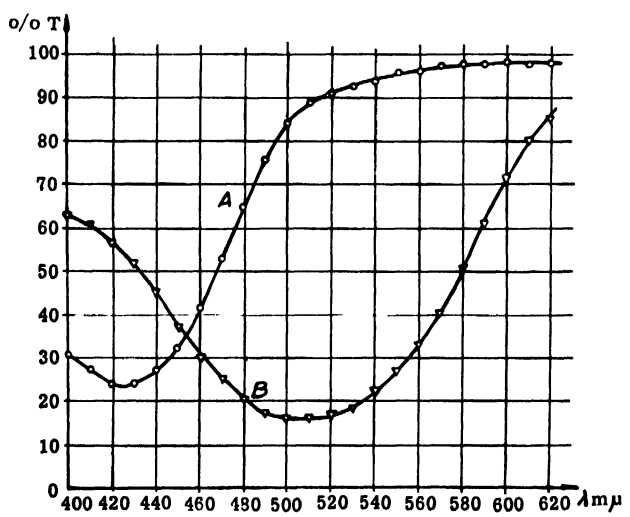
(*e*) Add 0.20 ml of hydrochloric acid (1:1) and bring up to volume.

(*f*) Determine the optical density at 525 mμ at the end of 30 minutes, against a blank with the same quantity of alizarine treated in the same fashion.

(*g*) Compute the quantity of zirconium by use of the calibration curve obtained with standards of known concentration.

All the measurements were carried out on a Unicam spectrophotometer model SP 500.

In order to choose the optimal wavelength for the determinations to be made, alizarine, quinalizarine and their respective zirconium compounds were used (Figs. 1 and 2). According to these figures, it will be seen that the wavelengths which are most convenient are: (*a*) for the determination of zirconium with alizarine-sulfonate: 525 mμ; (*b*) to determine zirconium with quinalizarine: 595 mμ.



Curve A : alizarine in water
Curve B : alizarine + 100 γ of Zr.

Figure 1

Table I

Sample	Paper pulp, gm	U retained, mg
1	ca 0.5	3.0
2	ca 0.5	2.5
3	ca 0.3	28.9

Table II

Sample	Containing		γ of Zr added	γ of Zr found
	Element	mg		
1	—	—	100	100
2	U	1000	100	111
3	U	1000	100	112
4	U	1000	100	100*
5	U	5000	100	98*
6	U	2000	100	101*
	Ti	0.2		
	Sn	0.2		
	V	0.2		
	Cr	0.5		
	Mo	0.5		
	W	0.5		
	Fe	1		
	Cu	0.5		
	Th	1		
7	Be	1000	10	10
8	Be	2000	10	8
9	Be	1000	100	96
	Fe	5		
	Al	2		
	Ca	5		
	Mg	5		
	Si	10		
10	Th	2	100	98
	Ce	2		
	La	2		
	Ti	2		
	Sn	2		
	Cr	1		
10	Fe	2		
	Mo	2		
	W	2		
	Cu	2		

* Double precipitation.

Following the calibration curves obtained with the two dyes (Figs. 3, 4, and 5) one can deduce that sensitivity for the alizarine and quinalizarine complexes is 0.013 γ/cm² respectively. Despite the greater sensitivity of the latter, sodium alizarine sulfonate is preferred to make it possible to operate in an aqueous medium.

The spectrophotometric determination of zirconium by the production of its alizarine complex is influenced by the presence of many elements.

A special study was made of the effects produced by uranium, beryllium, iron, and thorium, and the tolerable limit for the other elements was determined.

Influence of Uranium

It will be noted (Figs. 6 and 7), that the presence of uranium has a certain influence in zirconium colorimetry. From this, one may come to the conclusion that zirconium can be estimated in the presence

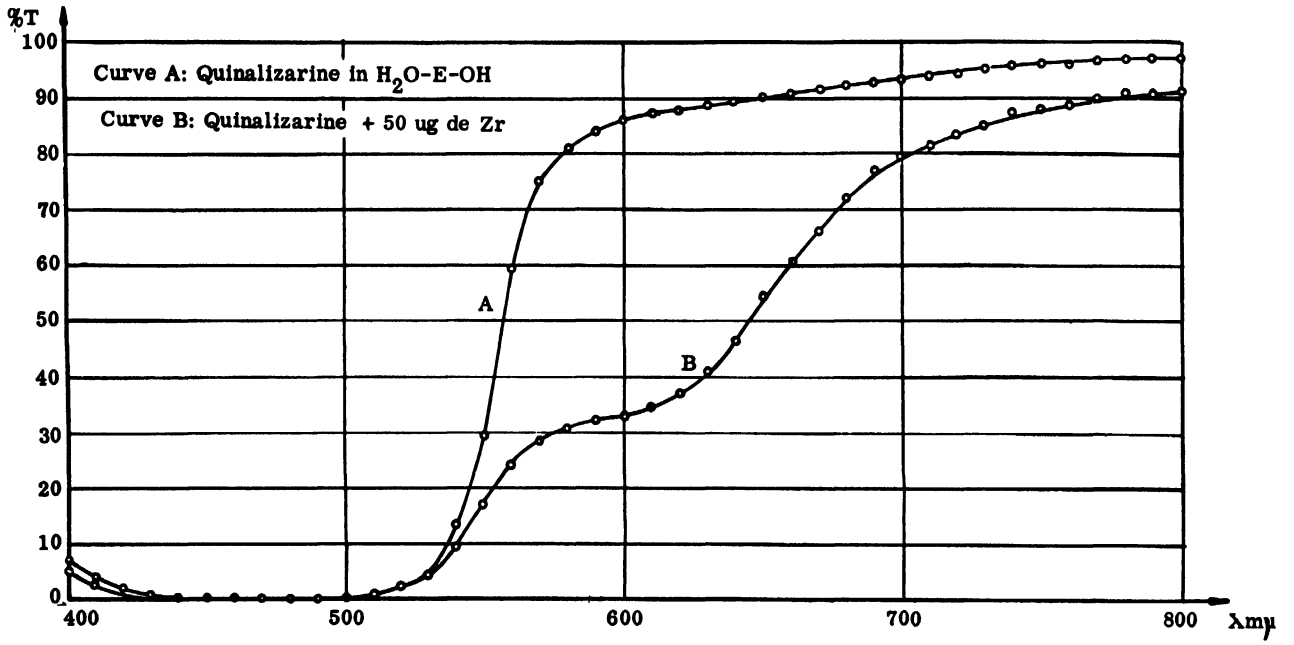


Figure 2

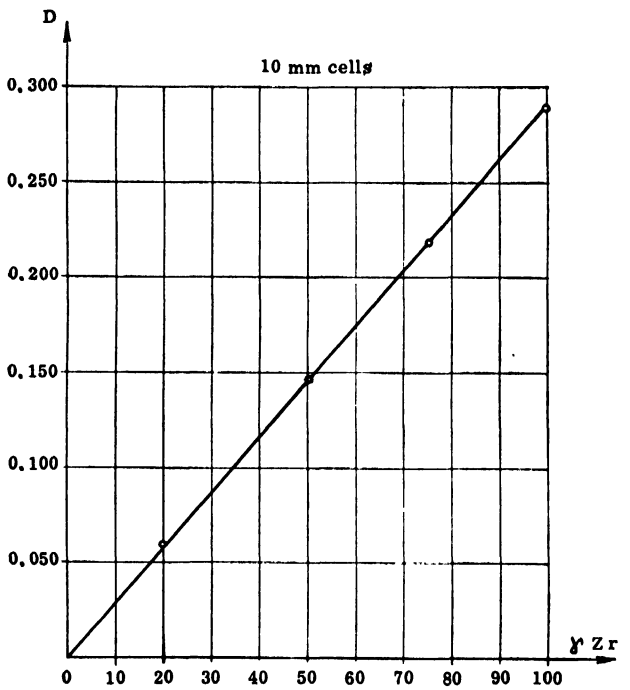
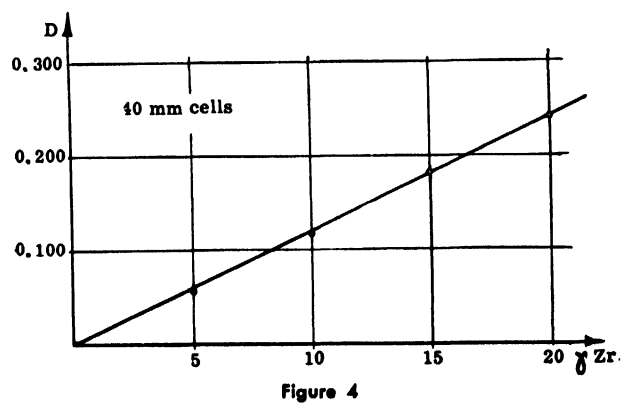


Figure 3



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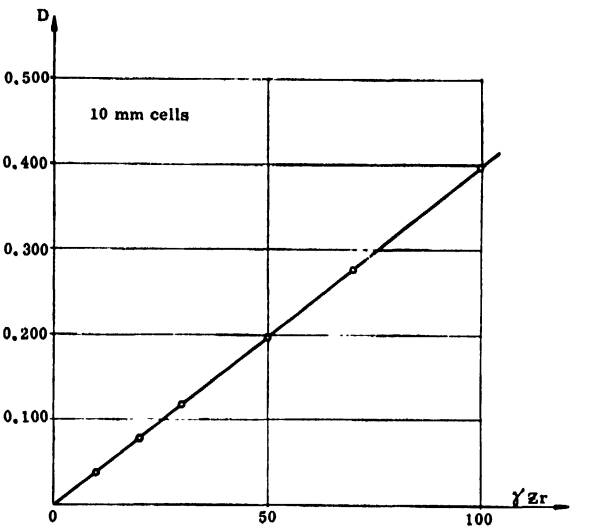

Figure 5

of uranium, as long as the reading is taken against a blank using the same quantity of uranium.

It is clear, from Fig. 6, that it is possible that the first fractions of uranium consume the excess of alizarine present in the solution, and for this reason, that more concentrated solutions of this element do not absorb proportionally more light. Thus, when zirconium is determined before separation of the uranium, it is necessary to carry out reprecipitation, in order to eliminate the small quantities of uranium which might be retained in the paper. On the other hand, when zirconium is determined in the presence of quantities of uranium greater than 0.1 gm, it is not of critical importance that the blank contain exactly the same quantity of the latter as does the sample, as long as the differences remain within a decigram.

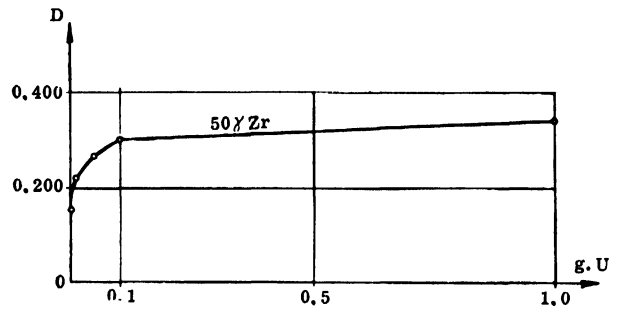

Figure 6

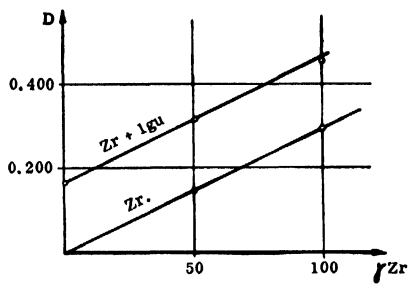

Figure 7

Influence of Beryllium

In the colorimetric determination of zirconium, quantities of the order of some mg of beryllium are not relatively disturbing. In tests carried out with up to 10 mg of beryllium, the error in the determination of 50 γ of zirconium was 3 γ in excess.

The quantities of beryllium which remain after separation of the zirconium with "pararsonic" acid were determined colorimetrically, and are those in Table III.

Table III

Sample	*Beryllium in the sample (gm)*	*Paper pulp (gm)*	*Beryllium retained (gm)*
1	0.5	ca 0.5	0.75
2	1.0	ca 0.5	1.50
3	2.0	ca 0.5	1.75

Influence of Iron

Iron, in the ferric form, has an appreciable influence. Being added to a solution containing alizarine, it produces a compound which absorbs light over a wide range of wavelengths. Figure 8 shows the absorption spectrum obtained with 10 mg of ferric iron and 2 ml of a 0.1% solution of sodium alizarine sulfonate in 25 ml. The influence this has at 525 mμ is considerable. The influence of iron can be eliminated by reducing it to the ferric form with a suitable reducing agent. Figure 9 shows the value obtained in a series of determinations using hydroxylamine hydrochloride and thioglycolic acid as reducing agents.

In general, it seems preferable to use the second, since it is not sought to regulate the acidity with special care.

Effects of Thioglycolic Acid

It has been verified, in the first place, that concentrations up to 1% in the final solution do not cause appreciable modifications in the values obtained for zirconium.

An investigation was made of the influence of thioglycolic acid with respect to uranium, iron and beryllium, which are the elements who presence is most frequent in the solutions in which zirconium is determined.

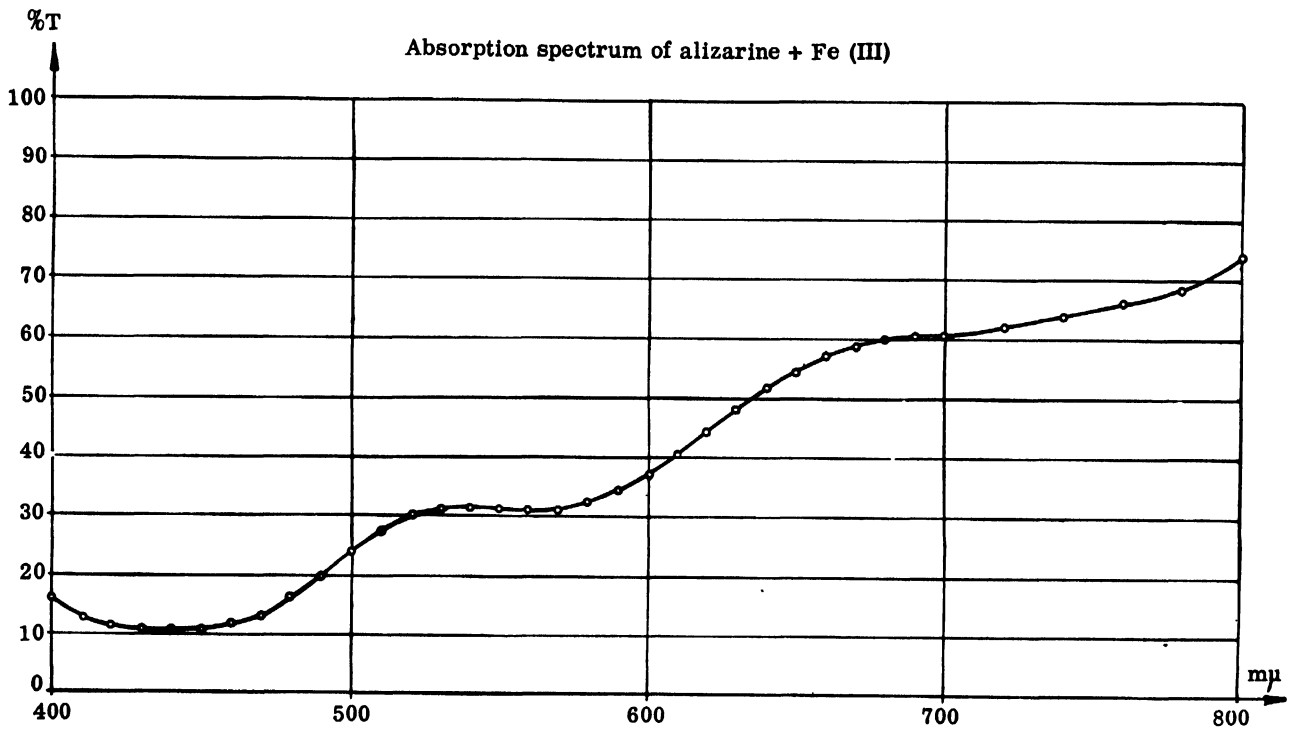

Figure 8

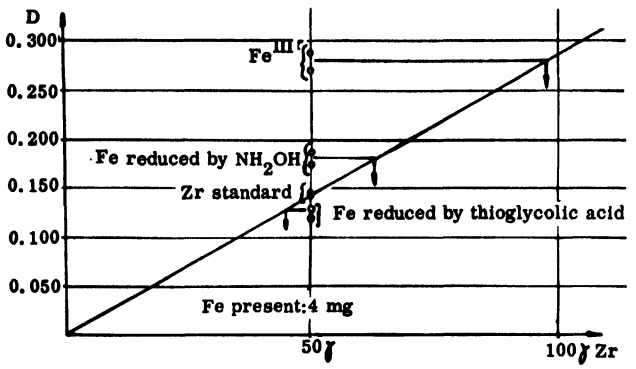

Figure 9

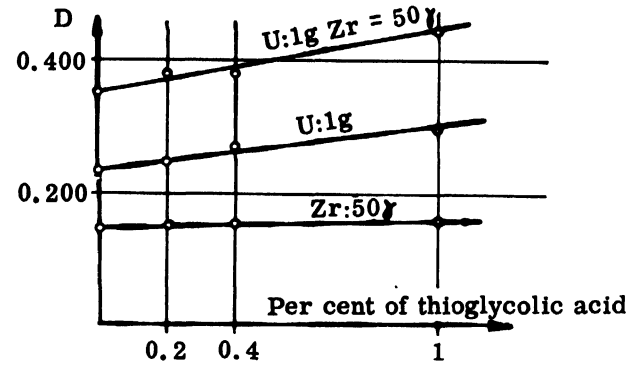

Figure 10

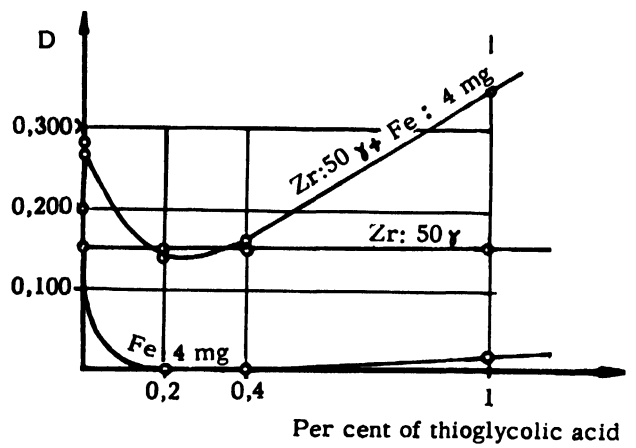

Figure 11

In the case of uranium, it is particularly important, since it is possible to evaluate the zirconium in its presence, and iron is one of the most common impurities. On Fig. 10, we show the values obtained as these points were investigated.

Thereafter, the influence of this reducing agent in systems using iron and iron-zirconium was reviewed. The results are shown on Fig. 11. The optimal concentration of thioglycolic acid, for quantities of the order of 4–5 mg of iron, is between 0.2 and 0.4%. It is worth noting that, above these concentrations, the values of the optical densities obtained for the zirconium-iron systems are abnormally high.

If there is some beryllium in the solutions in which zirconium is determined, the iron which may also be present cannot be reduced with thioglycolic acid. This is clear from a study of the curves shown on Fig. 12.

Influence of Thorium

According to Grimaldi and White[1] the thorium precipitates in very small proportions with pararsonic acid; these authors only find 5 γ of thorium dioxide in a test made with 10 mg. In the experiments carried out, these conclusions are confirmed for a few mg of thorium (see Table I). However zirconium might have to be determined in samples which are much richer in thorium, the coprecipitation of this element might then be significant, so that it is interesting to know the error which the presence of thorium causes in the determination of zirconium. In Table IV, we show the results obtained with mixtures of zirconium and thorium, by applying the colorimetric process with sodium alizarine sulfonate. It is demonstrated that a greater hydrochloric acidity, while it reduces the sensitivity of the reaction with respect to the zirconium, nearly totally eliminates the effect of up to more than 1 mg of thorium.

Influence of Other Elements

Other elements which interfere with the colorimetry of zirconium are shown in Table V.

CONCLUSIONS

(*a*) It can be shown that the precipitation of zirconium with pararsonic acid makes it possible to carry out efficient separation of the latter from quantities of uranium and beryllium running to a few grams.

(*b*) This separation is effective even in the presence of some milligrams of thorium, cerium, lanthanum,

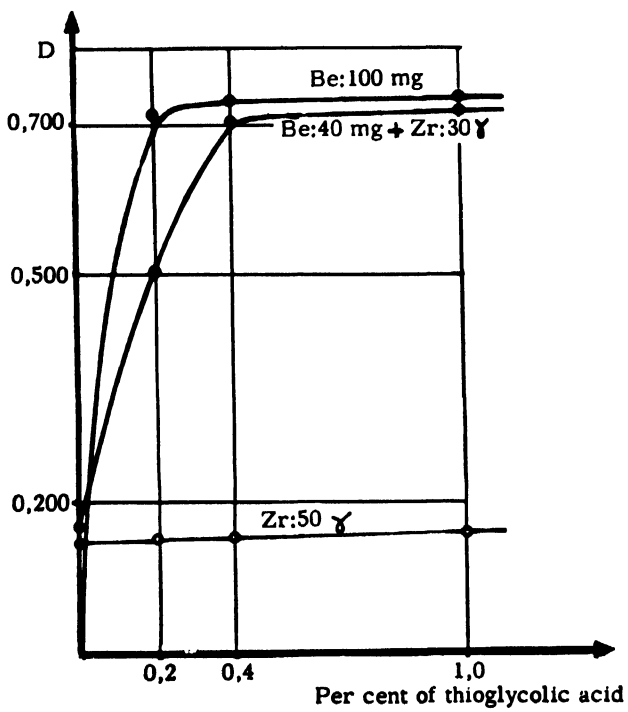

Figure 12

Table IV

Zr (γ)	Th (γ)	Acidity (N)	D
50	0	0.25	0.127
50	0	0.50	0.115
50	0	1.25	0.059
50	100	0.25	0.184
50	100	0.50	0.122
50	100	1.25	0.064
50	1200	0.50	0.213
50	1200	1.25	0.059

Table V

Zr added (γ)	Element added (γ)		Optical density
50	———		0.146
50	100	Ga	0.149
50	100	In	0.137
50	100	Tl	0.137
50	50	Ti	0.171
50	200	Ti	0.226
50	50	Sn	0.152
50	200	Sn	0.220
50	50	V	0.130
50	50	Cr	0.326
50	200	Cr	0.555
50	300	Mo	0.206
50	300	W	0.166
50	100	Sb	0.128
50	300	Cu	0.146

titanium, tin, copper, chromium, iron, aluminum, calcium, magnesium, molybdenum and tungsten.

(*c*) It can be shown that the direct colorimetry of zirconium is possible in the presence of uranium, if a blank is used having the same quantity of U.

(*d*) A study is made of the effect of uranium, iron, beryllium and thorium in the colorimetry.

(*e*) Thioglycolic acid is convenient to use to eliminate any interference from ferric iron, but it cannot be used in the presence of beryllium.

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Determination of Microquantities of Cadmium in Uranium

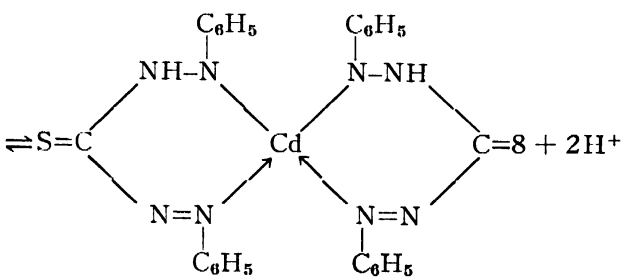
By Rafael H. Rodríguez Pasqués and Julia F. Possidoni de Albinati,*Argentina

Present chemical methods for determining traces of cadmium are divided into the polarographic[1] and the colorimetric[2] methods. Among the latter are nephelometric determination by precipitation as brucine iodocadmiate,[3] the decrease in absorption at 241 mμ for 1,10-phenanthroline due to the cadmium present,[4] and spectrophotometry of the red-colored compound of cadmium with diphenylthiocarbazone.[5-8]

We studied this last procedure and its application to the determination of cadmium in uranium. In general outline the technique follows that given by Rodden,[10] but we have considered the variables that notably affect the sensitivity of the method.

The Cd contained in a NaOH solution combines with diphenylthiocarbazone (dithizone) dissolved in carbon tetrachloride, producing a pink compound that is soluble in that solvent (cadmium dithizonate). The color intensity depends on the amount of Cd present, and is compared by spectrophotometry at 520 mμ.

$$2C_6H_5 - N = N - CS - NH - NH - C_6H_5 + Cd^{++}$$



The dithizone that does not combine with the Cd remains dissolved in the aqueous phase as an alkaline dithizonate, and hence its intense green color does not interfere. Denoting dithizone by DZH

$$DZH + NaOH \rightleftarrows NaDZ + H_2O$$

Dithizone can also combine with many other metals, but if the solution of the dithizonates is shaken with very dilute hydrochloric acid, which selectively decomposes Cd dithizonate, the latter metal passes into the aqueous phase, separating from the others, and under suitable conditions the color develops, the intensity being measured spectrophotometrically.

Original language: Spanish.

* National Atomic Energy Commission.

REAGENTS AND APPARATUS

The reagents and material employed, as well as the water used to prepare them, should be free of impurities capable of producing red dithizonates.

Ammonium citrate 50%: 79.3 gm of citric acid are dissolved in a small amount of water; concentrated ammonia is added, with stirring, until there is an incipient smell of ammonia (80–85 ml). It is cooled and diluted to 200 ml. This solution is purified by extraction with an 0.020% solution of dithizone until it is free of metals, i.e., to the point where, upon being shaken with portions of dithizone solution, the latter keeps its green color.

Ammonium citrate 10%: by dilution of the above with distilled water.

Concentrated ammonia: analytically pure.

Thymol blue indicator: 0.1 gm of thymol blue is dissolved in 2 ml of $N/10$ NaOH and 5 ml of 90% alcohol, and diluted to 250 ml with 20% alcohol.

Carbon tetrachloride: purified by distillation and washed with 20% sodium hydroxide; separated from the aqueous solution by passing through a filter moistened with carbon tetrachloride, and stored over caustic soda pellets.

Dithizone, 0.020%: 20 mg of diphenylthiocarbazone is dissolved in 100 ml of carbon tetrachloride, and shaken with 55 ml of 10% ammonium hydroxide. The organic layer is discarded and the residue is washed with 25 ml of carbon tetrachloride, which is also discarded.

Dithizone solutions of higher dilution: these are prepared from the above at the moment of use, diluting with carbon tetrachloride.

Hydrochloric acid $N/100$: by dilution of hydrochloric acid for analysis.

Standard cadmium solution: a mother solution containing 100 γ/ml, is first obtained by dissolving anhydrous cadmium sulfate (gentle heating) and then diluting to 1 γ/ml with $N/10$ hydrochloric acid.

Decanting flasks of Pyrex glass, 150 and 250 ml: Should be free of organic matter.

The spectrophotometer used was the Unicam SP 500 with 10 mm cells.

GENERAL PROCEDURE

The cadmium should have been extracted from the solution containing it. To this end, the solution is raised to a pH above 9.5 with ammonium hydroxide, using thymol blue as indicator; 5 ml of concentrated

ammonia are added, and it is diluted to 100 ml. It is repeatedly stirred in a 150 ml flask with 10–20 ml portions of 0.020% dithizone until one of these portions keeps its emerald color. The organic phases are separated.

All the organic extracts are combined in another flask and washed by stirring with 10 ml portions of distilled water (an auxiliary flask is used) until the aqueous phase remains colorless. The washings are discarded.

The organic solution, which may contain dithizonates of various metals, is stirred for a long time with a single 10 ml portion of $N/100$ hydrochloric acid. The organic phase is discarded; the cadmium remains in the aqueous phase, and may be accompanied by zinc, lead, thallium, and traces of copper and nickel.

The aqueous solution is washed with 5 ml portions of 0.002% dithizone solution, which extracts the metals as long as the washings are green. The washings are discarded. All the dithizone is eliminated by stirring with small portions of carbon tetrachloride until the solution is no longer green.

The cadmium should not remain in the form of the dithizonate for a long time, since dithizonate solutions and dithizone itself are not very stable. Accordingly, each of the substances or samples should be put through the process described above with no interruptions and be put aside temporarily upon reaching this point, so that the process may be recommenced with another sample.

At this point the cadmium is in 10 ml of $N/100$ hydrochloric acid. Color development is now performed: 5 ml of 10% ammonium citrate and exactly 5 ml of freshly-prepared dilute dithizone are added to the $N/100$ hydrochloric acid solution. A convenient concentration is 0.004%.

Five ml of 20% sodium hydroxide solution is added and the whole is stirred for a few seconds. This results in the formation of cadmium dithizonate, pink in color, dissolved in the carbon tetrachloride. The solution of cadmium dithizonate is passed rapidly through a dry filter paper into the cell, and then the optical density at 520 mμ is read by comparison with a blank without cadmium and with standard solutions containing known amounts of the metal that have undergone the same processing as the sample.

The spectrophotometer reading should be taken rapidly since the colors are not stable.

For this reason, as well as for others that will be set forth later, it is inappropriate to draw up a definitive photometric calibration curve.

The color intensity satisfies Beer's law, and therefore it suffices to add to the samples a single known substance containing cadmium, the extinction of which enables us to plot a straight-line function of the concentration of the metal.

DETERMINATION OF CADMIUM IN URANIUM

Since cadmium has a large capture cross-section for thermal neutrons, it is necessary to be able to determine amounts of the order of 10^{-7} gm/gm or less; in view of the fact that the method can detect one-fourth of one γ, some 3 gm of uranium must be worked with, if the latter is in a very pure state.

The uranium should be converted to uranyl nitrate or another uranyl salt, dissolved in very little water. In order to keep it in solution at the high working pH, 10 ml (or a larger volume, if required) of 50% ammonium citrate solution is added.

From this point on the general procedure is applied.

EXPERIMENTAL

Spectral Absorption of Cadmium Dithizonate (Cadmium 4 γ)

The red compound was obtained with the use of 0.004% dithizone. The readings were checked against a blank treated in the same way as the specimen containing cadmium. Results in Fig. 1.

Application of the Process to Pure Cadmium Specimens

The extinction straight line of Fig. 2 shows the applicability of the general method. Only metals present: cadmium and sodium.

Application of the Process to Specimens with Uranium Present

The results are given in Fig. 3. The first step was purification of a uranyl nitrate solution by dithizone, in the presence of ammonium citrate and ammonia, to eliminate any cadmium that might be present as an impurity. This purified uranium was then distributed among various specimens. Several experiments similar to the one described were performed, resulting in straight lines with varying slopes.

Influence of Light

We intended to plot a calibration curve, but the graphs obtained did not coincide; the cause of the

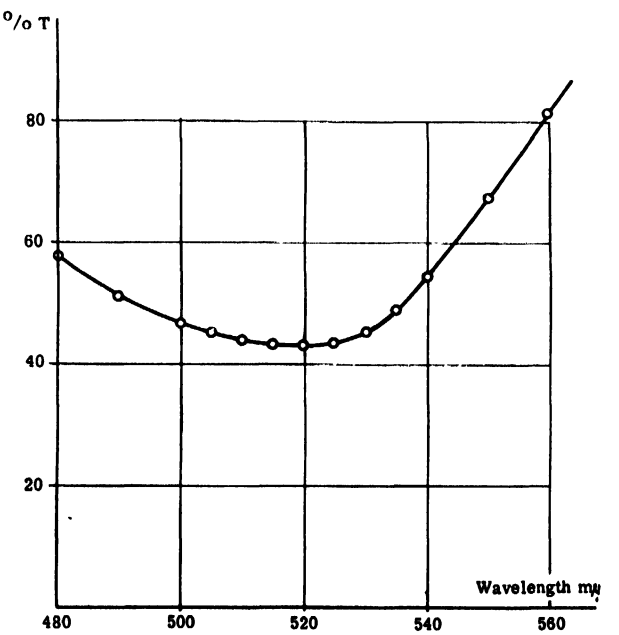


Figure 1

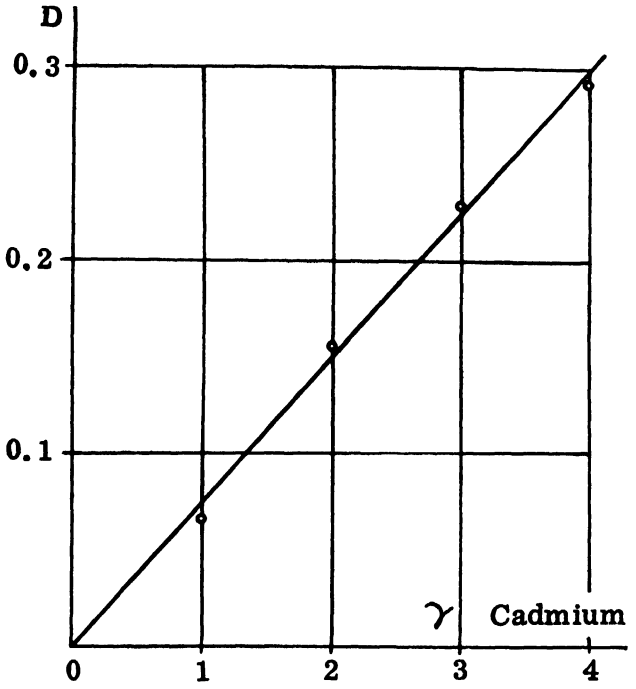


Figure 2

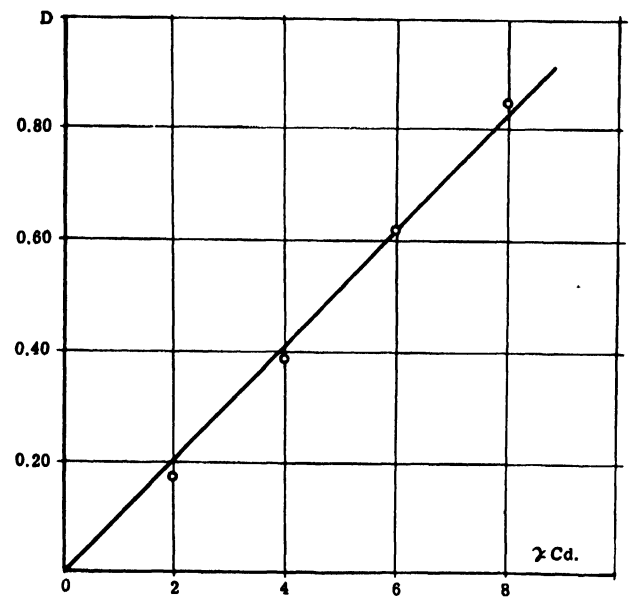


Figure 3

divergencies had to be found. The literature contains references to the instability of dithizone and the dithizonates to light.[11, 12, 13] Accordingly, this effect was studied with four identical "pure" specimens, each containing 5 γ of cadmium. Specimens I and II were always handled in strong light, and Specimens III and IV in the dark. The colors obtained were compared with a blank test, using carbon tetrachloride (Table I).

We see that the difference in illumination did not introduce any significant operational change under the prescribed conditions.

Variations in Uranium Concentration

It was found that the results do not depend on the uranium concentration, as is shown in Table II. In both series the uranium added was previously purified with dithizone. The colors were brought out with 0.004% dithizone.

Influence of the Dithizone Concentration

We have seen that as a rule the photometric curves do not coincide. One possible cause was that the color intensity produced might vary with the concentration of dithizone employed to develop it. It was found that this was actually the case, as is clearly brought out by the data of Table III and the corresponding Fig. 4.

The explanation for the influence of the reagent concentration lies in the fact that the reaction between the cadmium and the dithizone reaches a chemical equilibrium:

$$2DZH + Cd^{++} \rightleftarrows DZ_2Cd + 2H^+$$

The accumulation of high concentrations of dithizone tends to shift the reaction to the right: a higher dithizonate concentration is obtained, and hence a more intense color.

It is evident from Fig. 4 that low dithizone concentrations should not be used in this work, since they result in pale colors and since small variations in the concentration have more of an effect on the values of the corresponding transmittances. High

Table I

Specimens	*Cadmium*	*Light*	*T, %*
Blank	–	–	100
Specimen I	5γ	Strong	24.0
Specimen II	5γ	Strong	23.5
Specimen III	5γ	Weak	24.5
Specimen IV	5γ	Weak	24.5

Table II

Specimens (each containing 4 γ cadmium)	*Transmittances, % T*
Blank (no Cd)	100
0 gm uranium	37
2 gm uranium	36.5
4 gm uranium	38
6 gm uranium	37

Table III

Pair	*Cd solution (1 γ/ml) in N/10*	*N/10 HCl, ml*	*H_2O ml*	*Concentration of dithizone in CCl_4, %*	*10% citrate, ml*	*20% NaOH, ml*	*T, %*
A	–	4	6	0.001	5	5	100
	4	–	6	0.001	5	5	80
B	–	4	6	0.002	5	5	100
	4	–	6	0.002	5	5	51.5
C	–	4	6	0.004	5	5	100
	4	–	6	0.04	5	5	335.5
D	–	4	6	0.008	5	5	100
	4	–	6	0.008	5	5	30

concentrations of the reagent, on the contrary, give the dithizonate solution yellowish tones and make it necessary to operate with comparatively wide slits because the corresponding blanks are relatively dark (yellowish). Accordingly, 0.004–0.006% appear to be the most favorable concentrations.

Another set of experiments was devoted to a study of the variation of range of the method as a function of the concentration of the dithizone solution employed in the final phase of the process.

Three identical series of specimens containing cadmium were subjected to color development with 0.006%, 0.002% and 0.001% dithizone solutions (Fig. 5).

The curves show that linearity of concentration vs extinction no longer exist for diminishing percentages of cadmium as more dilute solutions of the reagent are employed.

Consequently, the values obtained and the range of the process depend on the variable under consideration. The same is true of the sensitivity; calculating the latter according to Sandell,[11] we find it to be 0.002 γ/cm^2.

Stability of the Colors Obtained

Our experimental work indicated that the intensity of the cadmium dithizonate color is not stable, as Sandell[11] has pointed out. Figure 6 represents the phenomenon over a period of time. Because of this instability the readings should be conducted without losing time, within five minutes after the color has developed.

The transmittances were measured against a blank that went through the entire process. T of the blank: 100% (cadmium content: 4 γ).

Dilution of the Cadmium Dithizonate Solution

We endeavored to find out whether Beer's law is satisfied, in order to determine whether it is admissible practice to dilute the solution in order to measure the transmittance in the event the colors obtained are too intense. We found that the dithizonate decomposed completely upon dilution with carbon tetrachloride and the green color of the reagent reappeared. The question then arose whether decomposition was due to the presence of some acid impurity in the solvent. We decided to wash the solvent with sodium hydroxide before using, and keep it thereafter in contact with pellets of sodium hydroxide. Correct data were obtained when this carbon tetrachloride was used as the diluent, as can be seen from Fig. 7 and 8, which refer to a cadmium dithizonate sample of "c" concentration, and to its dilutions to one-third and two-thirds with plain solvent and with

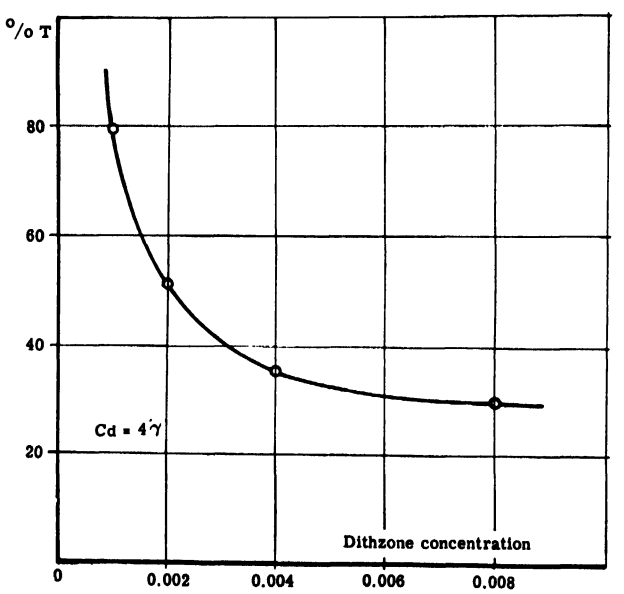


Figure 4

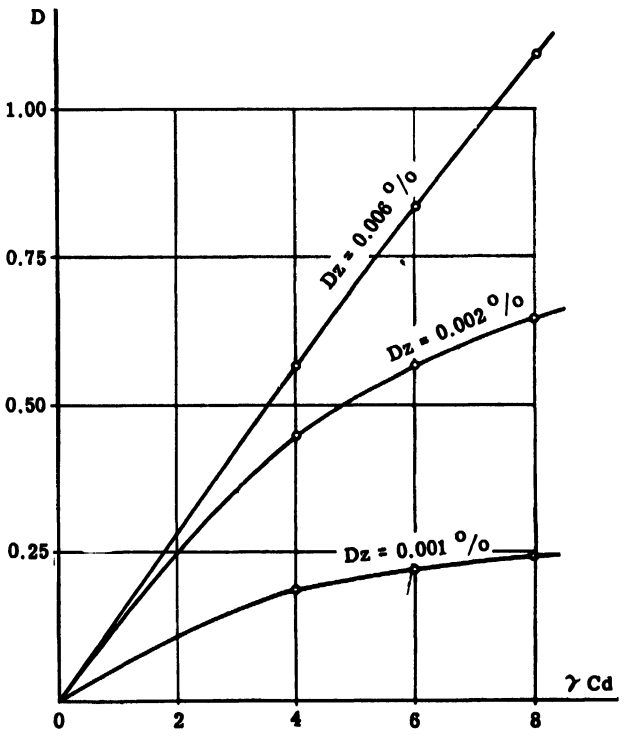


Figure 5

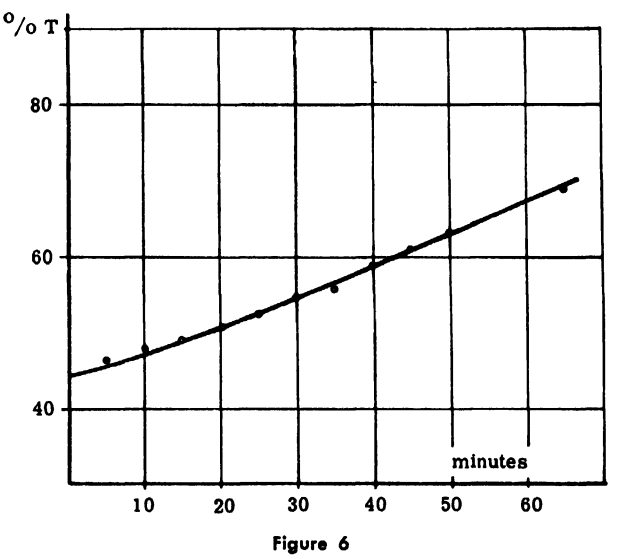


Figure 6

Table IV

	Transmittances, %	
	Series I	*Series II*
Blank	100	100
0 γ of Zn	35.5	42
200 γ of Zn	35	—
400 γ of Zn	37	41
600 γ of Zn	—	41

Table V

Specimens	*T, %*
Blank	100
4 γ cadmium	30.5
4 γ cadmium + 2 mg Tl	30.5

solvent washed with soda. The comparisons were made against a carbon tetrachloride blank. For both series, the measurements were repeated after a lapse of about 20 minutes in each case, the readings being used to plot the graph. This graph shows that although fading always occurs, it does so more slowly when washed carbon tetrachloride is used for dilution, the corresponding curve staying fairly close to Beer's law. Summing up, it is advisable and sometimes essential to wash the carbon tetrachloride with caustic soda, especially when it is to be used as a diluent.

Zinc Interference

The only interference possible at the high pH at which the cadmium dithizonate is formed is that of zinc.[10] We confined ourselves to verifying the fact that Cd:Zn ratios as high as 4:600 have no effect on the cadmium data obtained when uranium is present, as can be seen from Table IV.

Thallium Interference

Some procedures, differing from the one we explored, require a special modification if there is thallium present.[6] However, this is unnecessary when employing the technique with which the present paper deals. If there is thallium present alongside the cadmium, it interferes seriously (although its dithizonate decomposes quickly), but separation with $N/100$ hydrochloric acid effectively separates the cadmium from the thallium and prevents it from interfering. The following experiment (Table V) shows this. The specimens went through the entire process.

Selectivity of Decomposition of Cadmium Dithizonate with N/100 HCl

Upon extracting the cadmium in the presence of zinc, we found that all the cadmium dissolves in the $N/100$ hydrochloric acid in a single extraction, although the organic phase does not recover the emerald green color; in other words, in the presence of dithizonates of cadmium and zinc, for example, the acid selectively decomposes the cadmium dithizonate and extracts the ion all at once, even though the zinc is present in a much higher concentration.

This was formally substantiated by washing carbon tetrachloride solutions of dithizonates of cadmium and of zinc (cadmium: 4 γ; zinc 400 γ and 600 γ) with several portions of $N/100$ hydrochloric acid and developing the color of the cadmium dithizonate separately for each portion under suitable conditions. The only portions that contained cadmium were the first portion in each case, and the recovery of Cd was complete. In the thallium experiment as well, the cadmium is recovered quantitatively in a single extraction with 10 ml of $N/100$ acid.

CONCLUSIONS

A study was made of the dithizone method of determining traces of cadmium. It was observed that:

1. The concentration of the dithizone solution has an appreciable effect on the results in the final stage of the process.

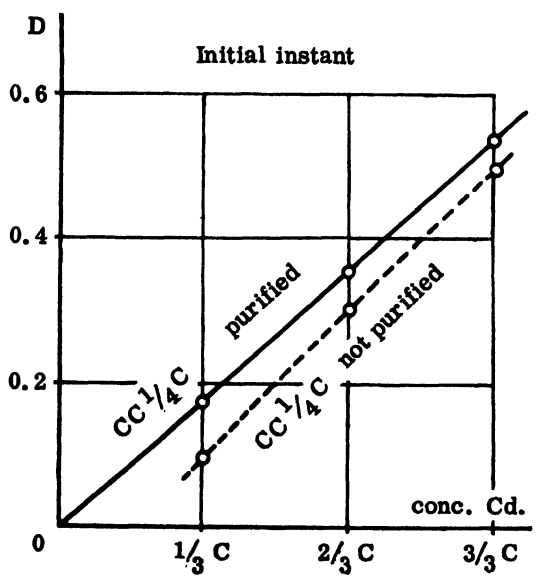


Figure 7

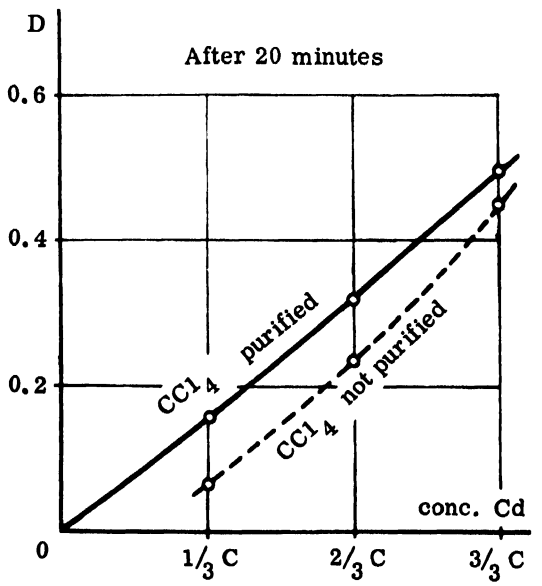


Figure 8

2. No calibration curve of permanent value can be constructed because of this fact and because of the instability of the solutions of the reagent.

3. The limits of the method's range also depend on the concentration of the reagent when the color is developed (hence it should not be below 0.004%).

4. It was found that zinc:cadmium ratios up to 150 : 1 and thallium : cadmium ratios up to 500 : 1 do not interfere with the results.

5. The following variables were also considered: influence of light, uranium concentration, and stability of the colors as functions of time.

Tables and graphs for the experimental data are included for each case. Practical recommendations are given for execution of the process.

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Determination of Uranium in Iron

By L. Kosta, Yugoslavia

For the purpose of investigating the distribution of uranium between iron and slag, obtained in the smelting of certain iron raw materials, a method was required by which it would be possible to determine traces of uranium in the metallic phase. A concentration of about 10^{-4}% U had been expected. One of the samples to be analysed was rich in chromium and contained also appreciable quantities of manganese and vanadium.

The 8-hydroxyquinoline method devised recently by Silverman *et al.*[1] would not meet the severe requirements imposed by a very low uranium level. The fluorimetric method could only be applied in the final determination of uranium.

The results obtained by the direct extraction procedure, described in a previous communication,[2] were discouraging as they disclosed only 50% recovery of uranium, probably because of the quenching effect of chromium and iron, coextracted to some extent in ethylacetate. The necessity for the removal of major components became evident.

The composition of the sample suggested the application of the mercury cathode by which iron, chromium, and partially manganese would be removed in one operation. The behaviour of uranium in solutions containing it in relatively large amounts (250 mg U/ml) has already been studied by earlier investigators,[3] but no data were available relating to the separation of large amounts of interfering elements from microgram quantities of uranium, on the mercury cathode.

To prove the feasibility of the separation, solutions of iron and chromium were prepared, approximating in composition to the solutions of the samples. Quantities of 5, 10, and 20 μg U were added and the electrolysis carried out.

The cell used was a slightly modified Mellaven cell (Fig. 1) which prevented the spraying of the solution and made the cooling very efficient. The current was 4–5 amp (0.3 amp/cm^2) and the electrolysis took 2 hours.

The method proved unsatisfactory when fluorescent discs were prepared directly from aliquots of the solution after electrolysis, but became very promising when extraction was applied at this stage. After electrolysis, some aluminum nitrate was added to the separated electrolyte and uranium carried down on aluminum hydroxide, precipitated with carbonate-free ammonia. The precipitate was dissolved in nitric acid and uranium extracted with ethyl acetate. Uranium was then stripped in water and diluted for the preparation of fluorescent discs.

The procedure finally adopted for the analysis of samples was as follows: 2 gm of the sample was dissolved by boiling with perchloric acid. The resulting solution was diluted to give a molarity of 1*M* in respect to perchloric acid. The solution was electrolysed for 2 hours at 4 amp. To the electrolyte were added 20 mg of aluminum as nitrate and uranium were coprecipitated on aluminum hydroxide with ammonia. After dissolution of the hydroxide

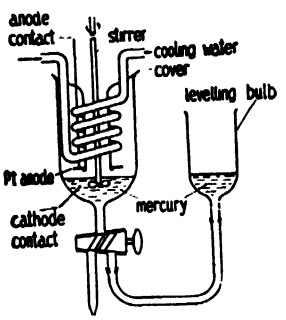

Figure 1

precipitate in 5 ml of 2*N* nitric acid and addition of 5 grams anhydrous aluminum nitrate to the solution in a separatory funnel, uranium was extracted with 10 ml of ethyl acetate. The solvent was then shaken with 10 ml of 1*M* sulphuric acid, the aqueous phase diluted to 25 ml in a measuring flask and fluorescent discs prepared with 1 gm of fluoride-carbonate mixture. The uranium content was determined with a transmission fluorimeter of increased sensitivity, designed in this laboratory.

The results obtained by the described procedure are given in Table I.

The recovery of over 90% of U at a very low concentration level makes the present method appear

Table I

Sample	Fe *added*	Cr *added*	U *added*	U *found*
Synthetic	1 gm	0.2 gm	5 μg	4.8 μg
Synthetic	1 gm	0.2 gm	10 μg	4.8 μg
Synthetic	1 gm	0.2 gm	20 μg	18.7 μg
Sample 1 (2 gm)	–	–	–	6.2 μg
Sample 1 (2 gm)	–	–	10 μg	15.6 μg
Sample 2 (2 gm)	–	–	–	11.0 μg
Sample 2 (2 gm)	–	–	10 μg	20.1 μg

to provide a satisfactory approach towards the solution of the problem. Its application could probably be extended to the determination of traces of uranium in materials whose major components can be deposited on the mercury cathode.

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Complex Formation Between Uranyl Ion and l-Ascorbic Acid

By Ivan J. Gal,* Yugoslavia

GLOSSARY OF SYMBOLS

The following symbols are used in this text:

H_2A, HA^-, A^{2-}	= ascorbic acid and its ion species, respectively,
c_A	= total concentration of ascorbic acid, M,
c_U	= total concentration of uranium, M
c	= $c_A + c_U$
μ	= ionic strength
[ ], ( )	= symbols for concentration and activity, respectively,
K_H	= apparent dissociation constant of ascorbic acid, (see Equation 1)
K	= dissociation constant of the complex, (see Equation 10)
M	= concentration, mol/liter
X	= molar fraction, c_U/c
λ	= wavelength in Ångstrom units
E	= extinction
E_D	= extinction of a solution of composition c_U and c_A measured against a reference solution of the same μ, pH and c_U, but $c = 0$.
$\epsilon_K \mid \epsilon_U$	= molar extinction coefficients of the complex and uranyl ion, respectively

A spectrophotometric study of the aqueous system uranyl ion-ascorbic acid showed that complex formation takes place. It was found that below pH 3, where the hydrolysis of the uranyl ion could be neglected, a weak complex of composition 1:1 is formed. The dissociation constant of the complex at $\mu = 0.1$ and at about 20°C was calculated. Above pH 3 other complexes are formed, but owing to the hydrolysis of the uranyl ion, the system could not be resolved.

The colored reaction between uranyl salts and *l*-ascorbic acid is used in the colorimetric determination of uranium,[1] and recently, ascorbic acid as supporting electrolyte was successfully applied for the polarographic determination of uranium in the presence of many other cations.[2, 3] The nature of this reaction, as far as we know, still remains unknown.

The aqueous system uranyl ion-ascorbic acid was investigated spectrophotometrically at constant ionic strength $\mu = 0.1$ ($NaClO_4$), at room temperature (20–21°C). From preliminary studies which involved absorption spectra measurements and pH-meter titrations, it could be concluded that complexes are formed in the pH range 1–10. Hexavalent uranium cannot be precipitated from aqueous solutions by ammonia or sodium hydroxide if ascorbic acid is present in a sufficient excess. A clear proof of complex formation is given in Fig. 1, which shows the extinction curves of uranyl perchlorate solutions in the presence and absence of ascorbic acid.

Unfortunately, above pH 3, the hydrolysis of the uranyl ion interferes with the study of the system, since pH > 3, equilibria between the uranyl ion and its hydrolysed species, all of which can be involved in the complex formation, must be taken into account. Obviously, such a system is far too complicated to be resolved merely by extinction- and pH-measurements. Thus, in the present work, only complex formation below pH 3 was investigated. The useful pH range in our investigation is very narrow; it lies within pH 2–3, since the concentration of the ligand (i.e., ascorbate ion, as shown later) is too low at pH < 2.

EXPERIMENTAL

Reagents

All reagents used were of Analytical Grade. $NaClO_4$ was prepared from stoichiometric quantities of $NaHCO_3$ and $HClO_4$. The salt was twice recrystallized and a 1M stock solution prepared. The $NaClO_4$ concentration was determined via Na_2SO_4. A 0.02M stock solution of $UO_2(ClO_4)_2$ was prepared from stoichiometric quantities of UO_3 and $HClO_4 \cdot UO_3$ was a very pure sample obtained from $UO_2(NO_3)_2$, purified by ether extraction. Uranium in the stock solution was determined gravimetrically. Crystalline *l*-ascorbic acid, obtained from E. Merck, Darmstadt (M.P. 189.5–190.5°C, titration with NaOH gave 99.8%), was not further purified. As ascorbic acid solutions are easily oxidized, no stock solutions were prepared, but weighed amounts of the acid were directly added to the solutions under examination.

Measurements

pH measurements were done as described in a previous work.[4] Extinctions were measured by means of a Hilger "Uvispek" spectrophotometer. The

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color developed in solutions containing UO_2^{++} and ascorbic acid is not very stable. Above pH 3.5, a constant fading was observed. This is probably due to the oxidation of *l*-ascorbic acid, catalyzed in the presence of uranyl ions. In neutral and alkaline solutions, the extinctions decrease rapidly and no exact measurements could be done. In acidic solutions, below pH 3.5, the color is quite stable; at least 30 minutes after addition of ascorbic acid no significant changes in extinctions occur. Measurements were carried out 8–15 minutes after addition of ascorbic acid, and, as a rule, accurate timing of measurements was done. In some cases it was necessary to correct readings for the initial value. All measurements were carried out at 20–21°C, at ionic strength $\mu = 0.1$. The ionic strengths and pH of solutions were regulated by addition of $NaClO_4$ and $HClO_4$ (or NaOH), respectively.

RESULTS AND DISCUSSION

Some preliminary studies concerning the dissociation of *l*-ascorbic acid as well as the hydrolysis of uranyl perchlorate were first undertaken. The dissociation of ascorbic acid was studied in an earlier paper,[4] from which an apparent constant K_H defined as

$$K_H = \frac{(H^+)\,[HA^-]}{[H_2A]} = 8.5 \times 10^{-5}\,M \qquad (1)$$

and valid at $\mu = 0.1$ (20–30°C), will be used here in numerical calculations.

The hydrolysis of uranyl ion was studied spectrophotometrically and by pH-titrations. It was found, in agreement with Sutton,[5] that below pH 3, mainly UO_2^{++} exists in perchlorate solutions; other ionic species due to hydrolysis can be neglected. In Fig. 2, molar extinction coefficients ($4 \times \epsilon_U$) of UO_2^{++} in perchlorate solution at different pH-s are plotted against wavelengths. It can be seen that only slight differences occur between curves at pH 2 and 3, but from the curve at pH 4 it can be concluded that the hydrolysis of UO_2^{++} is considerable.

The dependence of the extinction upon pH of a solution of $UO_2(ClO_4)_2$, containing ascorbic acid in large excess, is shown in Fig. 3. From the shape of the curves one may suppose that at least two complexes are formed in the pH range 2–5. Complex formation is, obviously, greatly influenced by the pH of the solution. The absorption of ascorbic acid and UO_2^{++} is negligible, hence the curves represent extinctions which are due to complex formation. Above pH 5, no exact measurements could be done, owing to the rapid fading of solutions.

Some information concerning the composition and the stability of complexes was obtained by the molar ratio method, as can be seen from Figs. 4, 5 and 6. In the ultraviolet, below 3000Å, the peak of ascorbic acid (Fig. 5) is a little shifted towards shorter wavelengths, but no further significant changes due to complex formation can be noticed. Above 3000 Å, the extinction curves of the complexes differ from those of ascorbic acid and UO_2^{++}. Ascorbic acid does not absorb above 3300 Å, but the uranyl ion has a characteristic band within 3900–4300 Å (Figs. 1 and 2). The extinction curves due to the complex formation do not possess the "uranyl band," but a rather intense over-all absorption, decreasing towards longer wavelengths. From the "molar ratio" curves one can conclude that complexes are dissociated to a large extent. Moreover, the plot of extinctions against molar ratios in Fig. 7 shows a definite inflection at molar ratio 1, suggesting that a complex of the composition 1:1 may be formed.

This was further confirmed by Job's method of continuous variation, carried out at pH 4.00, 3.32, and 2.90. The total concentration of the components was always $c_A + c_U = 4 \times 10^{-3}\,M$, $\mu = 0.1$. Job's curves are shown in Fig. 8. E_D values are plotted against the molar fraction $X = c_U/(c_A + c_U)$ in the wavelength range 3500–4500 Å, where ascorbic acid does not absorb.

As seen from Fig. 8, a 1:1 composition of the complex was obtained at all wavelengths and pH under examination. In general, Job's method gives reliable results only if one complex is formed. This is quite uncertain at pH 4.00 and 3.32 as beside UO_2^{++}, its hydrolysed-ion species could also be involved in the complex formation. But at pH 2.90, the hydrolysis of UO_2^{++} can be neglected, so that only one uranium ion, i.e., UO_2^{++}, can take part in the complex formation. The dependence of the extinction upon pH suggests that ascorbate ion HA^-) should be the ligand in question. (The ion A^{2-} can be neglected below pH 7.) Thus, we shall suppose that the following reaction takes place (below pH 3):

$$UO_2^{++} + HA^- \rightleftharpoons [UO_2HA]^+ \qquad (2)$$

The complex $[UO_2A]^+$ and/or polynuclear complexes of the type $[UO_2HA]_n^{+n}$ are not expected below pH 3.

To ascertain that Equation 2 represents the main complex formation in acidic solutions at pH < 3, the dissociation constant of the complex was evaluated, and its constancy checked on several solutions. This was done in the following way:

If Equation 2 holds, the extinction of any solution containing $UO_2(ClO_4)_2$ and ascorbic acid, is given by

$$E = [UO_2^{++}]\epsilon_U + [UO_2HA^+]\epsilon_K \qquad (3)$$

E is measured at a wavelength where ascorbic acid does not absorb (for example at any wavelength above 3300 Å), supposing 1-cm cells.
Further,

$$c_U = [UO_2^{++}] + [UO_2HA^+] \qquad (4)$$

$$c_A = [H_2A] + [HA^-] + [UO_2HA^+] \qquad (5)$$

or, using Equation 1:

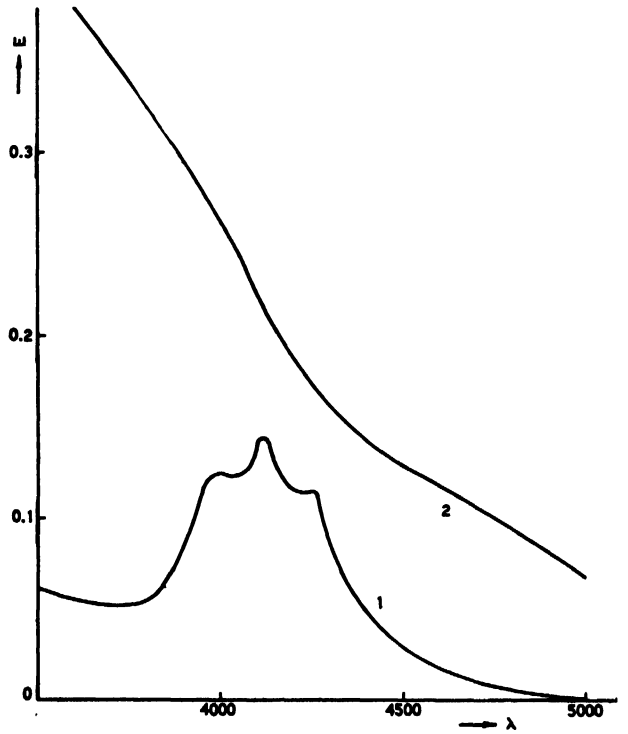

Figure 1. Curve 1: 4×10^{-5}M $UO_2(ClO_4)_2$. 4 cm quartz cells. pH = 4. Curve 2: 1×10^{-5}M $UO_2(ClO_4)_2$. 2×10^{-5}M ascorbic acid. 1 cm quartz cells. pH = 4. Ref. sol.: 0.1M $NaClO_4$

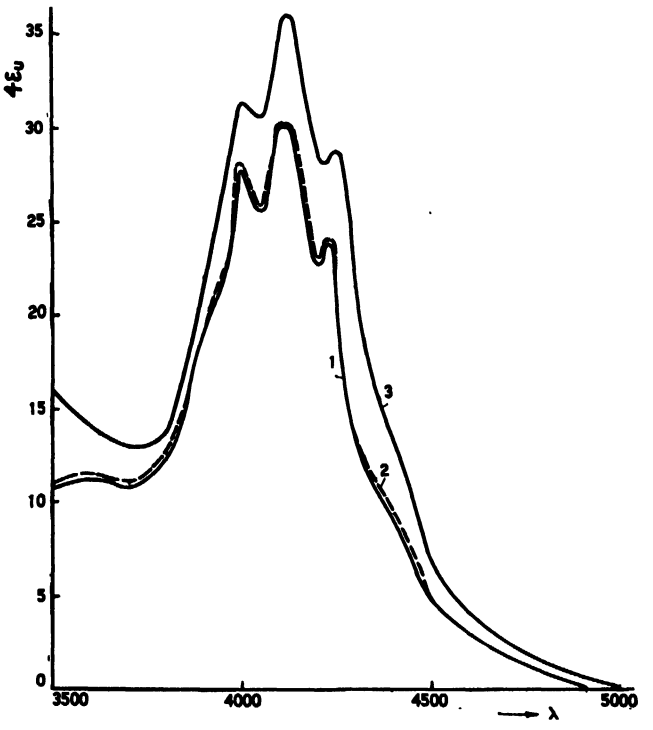

Figure 2. Curve 1: pH = 2. Curve 2: pH = 3. Curve 3: pH = 4. μ = 0.1 (perchlorate solutions)

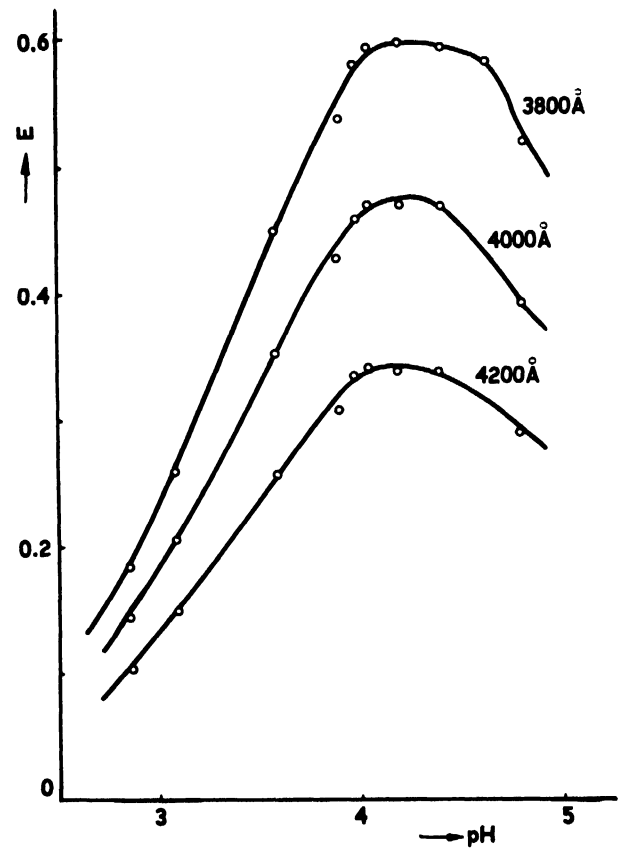

Figure 3. $c_U = 1 \times 10^{-4}$, $c_A = 2 \times 10^{-2}$, μ = 0.1. Ref. sol.: $c_A = 2 \times 10^{-2}$, $c_U = 0$, μ = 0.1

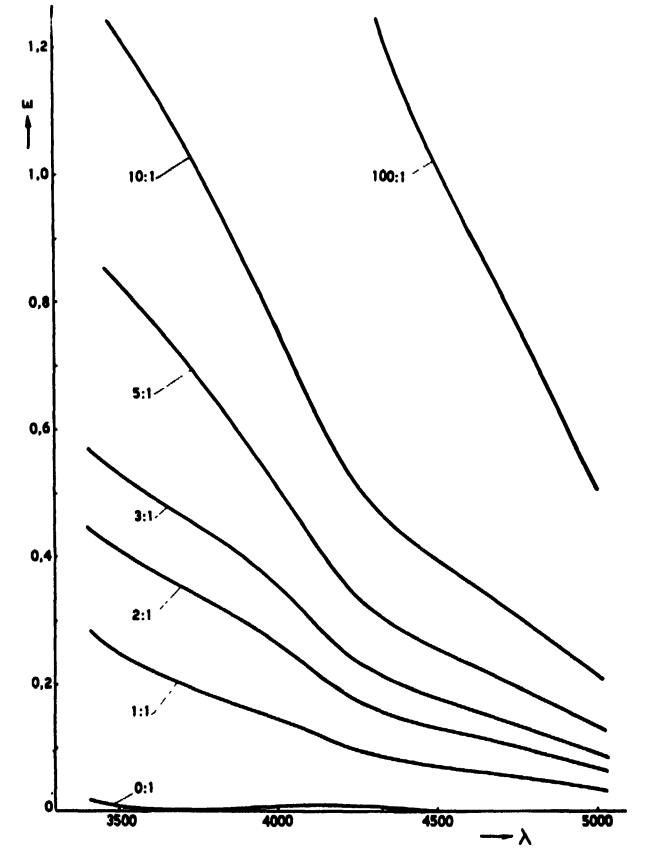

Figure 4. pH = 4. μ = 0.1. $c_U = 1 \times 10^{-5}$M. c_A/c_U is indicated on each curve. Reference solutions 0.1M $NaClO_4$. 1 cm quartz cells

$$[HA^-] = (c_A - [UO_2HA^+]) \frac{K_H}{K_H + (H^+)} \quad (6)$$

If the extinction is measured against a reference solution having the same c_U, but without ascorbic acid, then E_D is obtained:

$$E_D \equiv E - c_U\epsilon_U = [UO_2^{++}]\,\epsilon_U + [UO_2HA^+]\epsilon_K - c_U\epsilon_U \quad (7)$$

By combining Equations 4 and 7, it follows:

$$[UO_2HA^+] = \frac{E_D}{\epsilon_D} \quad (8)$$

where

$$\epsilon_D = \epsilon K - \epsilon_U \quad (9)$$

Thus, the dissociation constant of the complex equals

$$K \equiv \frac{[UO_2^{++}][HA^-]}{[UO_2HA^+]} =$$

$$\left[c_U - \frac{E_D}{\epsilon_D}\right]\left[c_A - \frac{E_D}{\epsilon_D}\right]\left[\frac{K_H}{K_H + (H^+)}\right]\left[\frac{E_D}{\epsilon_D}\right]^{-1} \quad (10)$$

K is a "concentration" constant which will be evaluated at $\mu \cong 0.1$. To simplify the calculation, let

$$\frac{K_H}{K_H + (H^+)} = \alpha \quad (11)$$

If ascorbic acid is added in a large excess, so that $c_A >> c_U$, then $(c_A - E_D/\epsilon_D) \cong c_A$. Hence,

$$K = c_U\epsilon_D \frac{c_A\alpha}{E_D} - c_A\alpha \quad (12)$$

Let $c_A\alpha = Y$; $c_A\alpha/E_D = X$. By plotting Y as function of X at constant wavelength and constant c_U, but varying c_A and pH of solutions, a straight line is obtained:

$$Y = \epsilon_D c_U X - K \quad (13)$$

where the intercept on the Y-axis equals $-K$, and from the slope of the line ϵ_D can be calculated. X and Y are easily computed by measuring E_D and pH of the solutions if c_A and K_H are known. Using Equation 13, K and ϵ_D were calculated at six different wavelengths by measuring E_D of solutions of different pH and c_A values. This is shown graphically in Fig. 9. Of course, owing to the inevitable experimental errors, the six lines in Fig. 9 do not intersect the Y-axis in one point. K and ϵ_D can be found out

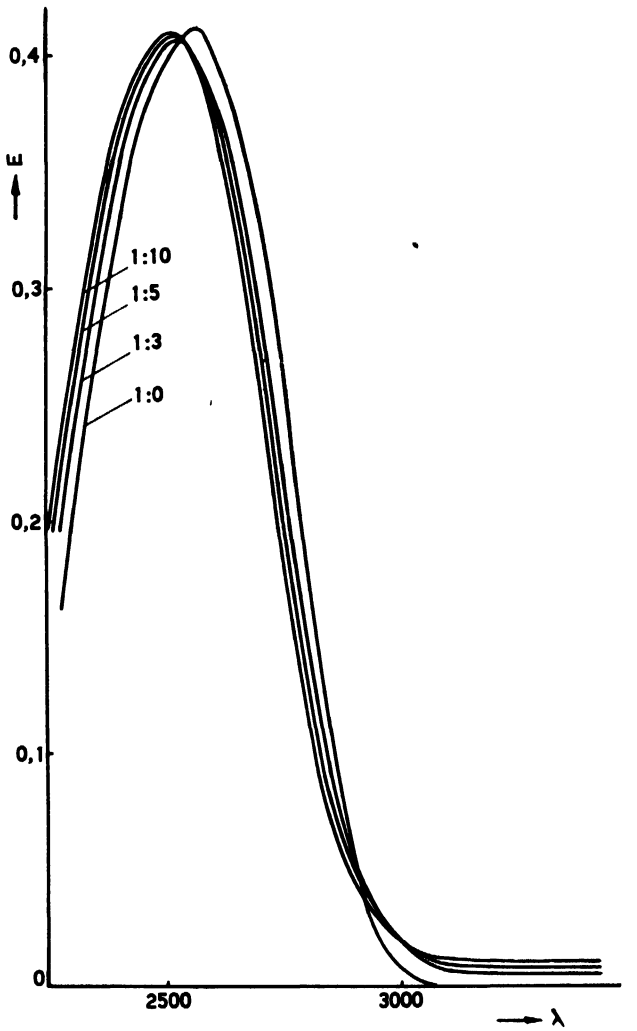

Figure 5. pH = 4. μ = 0.1. $c_A = 1 \times 10^{-4}$M. c_A/c_U is indicated on each curve. Measured against solutions of the same composition, but of c_A = 0. 0.5 cm quartz cells

graphically, but the algebraic method is more reliable. For this purpose, the well-known "least squares" method was applied. The required numerical computations were done using a calculating machine. All data are given in Table I; the results are tabulated in Table II. Only in one case, at pH 2.86, the X-values were too low and were disregarded. This was probably due to a slight hydrolysis of UO_2^{++} at a pH which is quite near 3. Data in Table I are average values of at least two measurements. In the last column of Table II, the corrected average values of $4\epsilon_D$ are tabulated (4 ϵ_D can be directly substituted in Equation 13, because 4-cm cells were

Table I*

No.	$(H^+)\times10^5$	$c_A\times10^3$	c_U	3600 Å	3800 Å	4000 Å	4100 Å	4200 Å	4400 Å
1	1.37	2.00	1×10^{-4}	0.222	0.184	0.146	0.125	0.105	0.083
2	1.64	3.00		0.269	0.223	0.177	0.151	0.126	0.099
3	1.88	4.00		0.302	0.252	0.199	0.169	0.143	0.113
4	2.06	5.00		0.328	0.272	0.214	0.182	0.154	0.121
5	2.24	6.00		0.350	0.291	0.229	0.194	0.164	0.129
6	2.55	8.00		0.386	0.319	0.251	0.214	0.179	0.142

* μ = 0.1. 4 cm cells. $K_H = 8.5 \times 10^{-5}$ M.

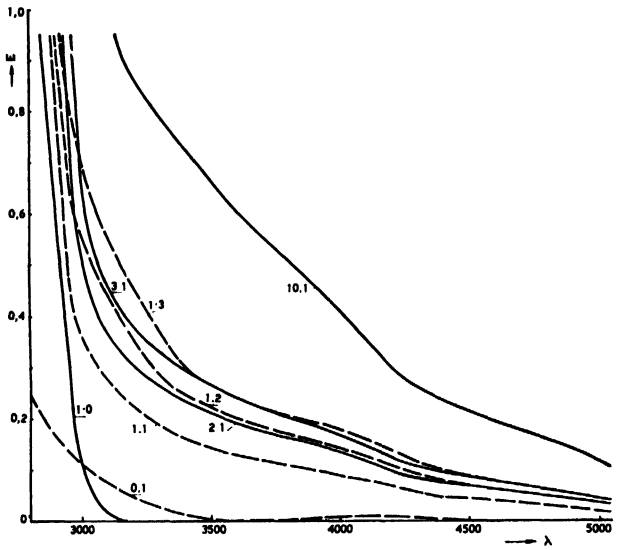

Figure 6. pH = 3.4 μ = 0.1. Fulldrawn curves: $c_U = 1 \times 10^{-3}$M. Dotted curves: $c_A = 1 \times 10^{-3}$. c_A/c_U given on each curve. Reference solutions 0.1M $NaClO_4$. 2 cm quartz cells

Table II

λ	$K \times 10^{+3}$	Average	Corrected $4\epsilon_D$
3600	3.68		8630
3800	3.38		7170
4000	3.17	$K =$	5650
4100	3.17	3.3×10^{-3}	4810
4200	3.14		4050
4400	3.29		3190

Table III

λ	ϵ_K	ϵ_U
3600	2160	2.8
3800	1795	3.1
4000	1426	7.0
4100	1210	7.5
4200	1018	5.7
4400	800	2.3

always used). The dissociation constant of the complex is given by $K = 3.3 \times 10^{-3}$ M valid at $\mu = 0.1$ and about 20°C.

From the last column in Table II the molar-extinction coefficients of the complex were calculated according to Equation 9. They are tabulated and compared with the molar-extinction coefficients of UO_2^{++} in Table III.

Using the $4\epsilon_D$ values for six wavelengths (Table II), the constancy of K was rechecked on several solutions of different c_A, c_U and pH, where the restriction $c_A >> c_U$ was not valid. The dissociation constant K was calculated according to Equation 10. Some of the results which were obtained are shown in Table IV.

In all cases, the dissociation constant was within $(3.3 \pm 0.3) \times 10^{-3}$, confirming thus the reaction postulated in Equation 2. The reaction given in

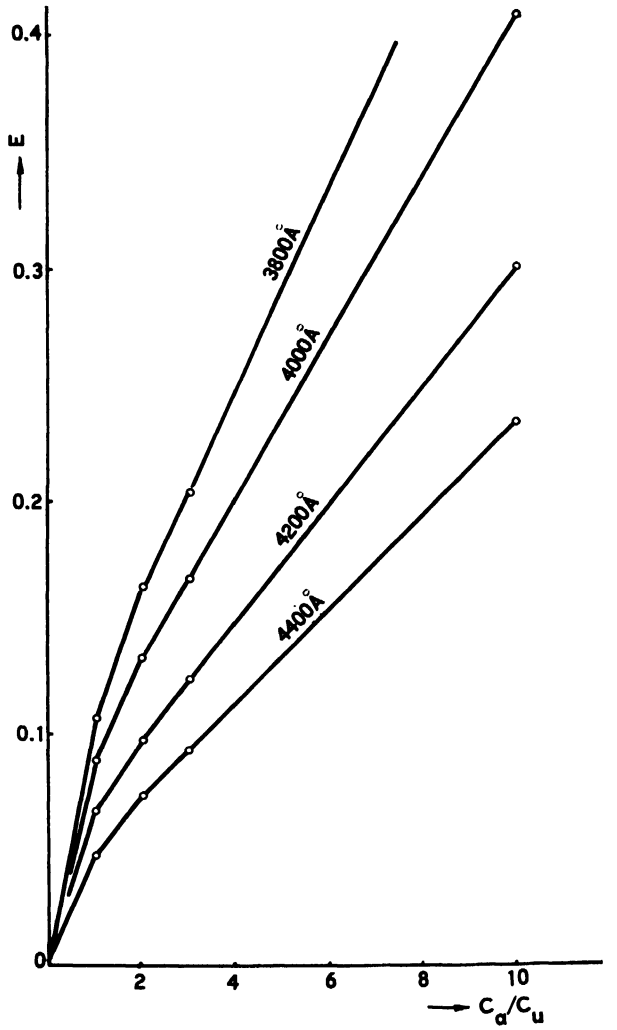

Figure 7. pH = 3.4. μ = 0.1. Reference solutions and cells as in Fig. 6

Table IV*

(H^+), c_A, c_D	E_D	λ	$K \times 10^3$
$(H^+) = 1.26 \times 10^{-3}$	0.623	3600	3.3
$c_A = 2 \times 10^{-3}$	0.523	3800	3.2
$c_U = 2 \times 10^{-3}$	0.411	4000	3.2
	0.348	4100	3.3
	0.295	4200	3.2
	0.235	4400	3.2
$(H^+) = 1.38 \times 10^{-3}$	0.504	3600	3.4
$c_A = 1 \times 10^{-2}$	0.420	3800	3.4
$c_U = 4 \times 10^{-4}$	0.336	4000	3.3
	0.286	4100	3.3
	0.241	4200	3.3
	0.186	4400	3.4
$(H^+) = 2.00 \times 10^{-3}$	0.480	3600	3.4
$c_A = 5 \times 10^{-3}$	0.401	3800	3.4
$c_U = 1 \times 10^{-3}$	0.330	4000	3.3
	0.285	4100	3.2
	0.239	4200	3.2
	0.181	4400	3.4
$(H^+) = 3.47 \times 10^{-3}$	1.100	3600	3.3
$c_A = 2 \times 10^{-2}$	0.934	3800	3.2
$c_U = 1 \times 10^{-3}$	0.750	4000	3.1
	0.641	4100	3.1
	0.536	4200	3.1
	0.417	4400	3.2

* μ = 0.1. 4-cm cells. For $4\epsilon_D$ see Table II.

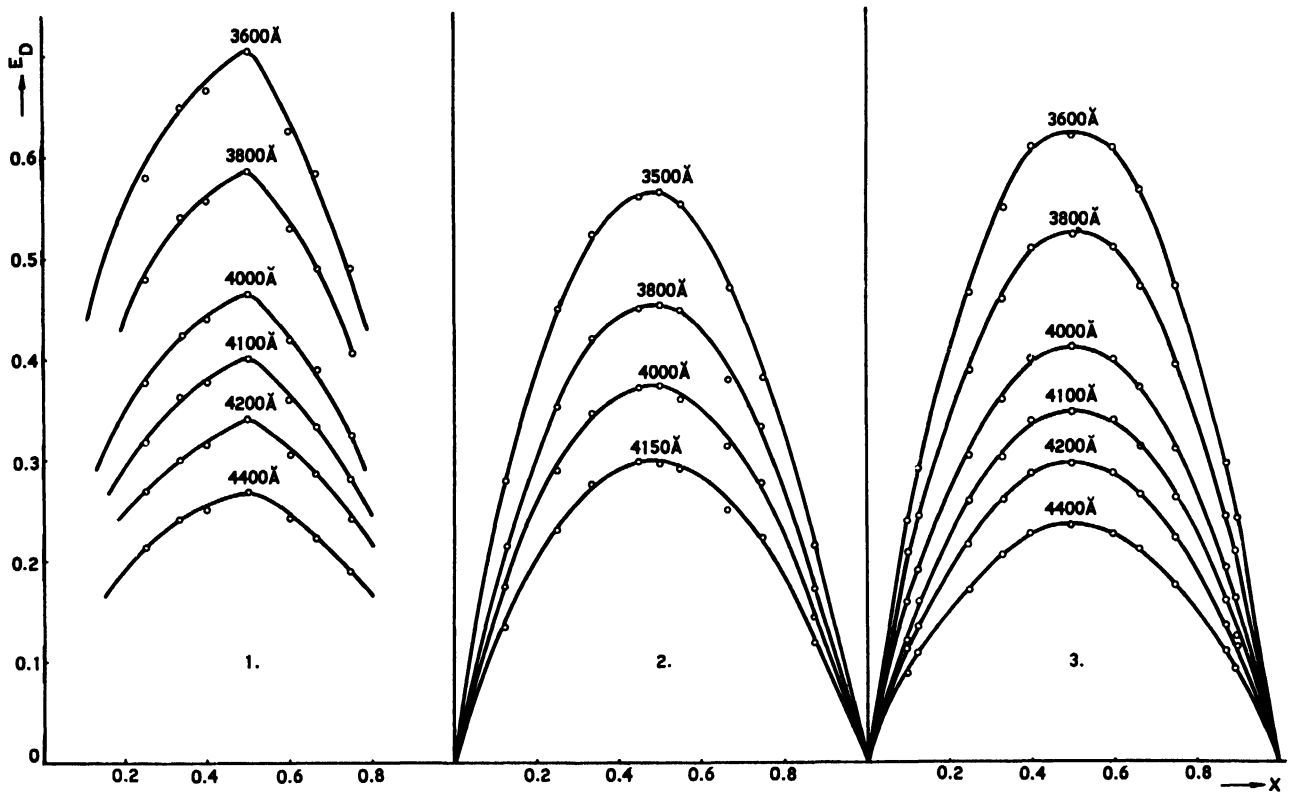

Figure 8. (1) pH = 4.00. 1 cm cells. (2) pH = 3.32. 2 cm cells. (3) pH = 2.90. 4 cm cells

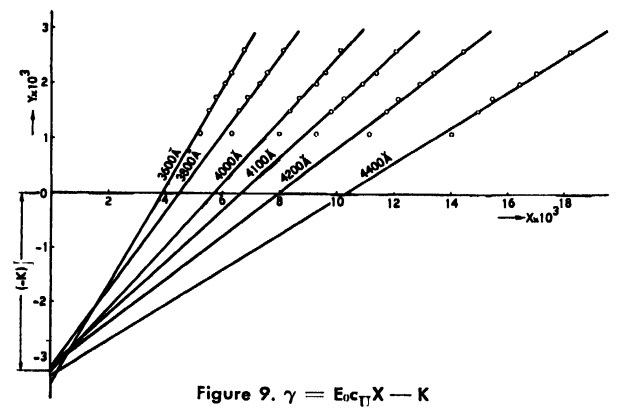

Figure 9. $\gamma = E_0 c_\Pi X - K$

Equation 2 must be considered only as the first step in the complex formation which takes place between UO_2^{++} and ascorbic acid. Above pH 3, obviously other complexes are formed, but, as mentioned, they could not be identified owing to the hydrolysis of the uranyl ion.

ACKNOWLEDGEMENT

Thanks are due to Professor P. Savić for the interest and support he gave during the work.

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Contribution to the Study of the Method and Factors Affecting the Spectrophotometric Determination of Traces of Boron with Carmine in Uranium Compounds

By R. Fernández Cellini and L. Gascó Sánchez,* Spain

Among the analytical methods used for the determination of the presence of small quantities of boron, the spectrophotometric techniques certainly are the most notable ones.

A great many organic reagents have been used, especially anthraquinone derivatives, since they readily form strongly colored compounds with boric acid.

Chronologically, let us list curcumin,[1-10] quinalizarine,[11-21] alizarine blue, [14-22] chromotrope 2B,[23] Solvay purple base,[14] diatrimide, [15,24-27] carmine,[28-31] carminic acid, [29] alizarine red (sodium salt of alizarine monosulfonate),[32-34] tetrabromochrysazin,[35] diamino anthrarufin, diaminochrysazin, tribromoanthrarufin and dicyanoquinalizarine.[36]

In most determinations made with the reagents mentioned above, it is necessary to separate the boric acid from its accompanying compounds, since they interfere with spectrophotometric determinations. Normally, distillation of the corresponding methylboric ester is used. The complications brought in by this distillation (efficiencies, contaminations, etc.) strongly urges, for the low concentrations, the use of a reagent as specific as possible, which would require no prior separations.

Among these, the most notable is carmine red, which has been used under these conditions by various researcher workers.[29-31]

All this finds application in the determination of boron in steel products, waters, soils, plants, biological materials, etc.

Cypres and Leherte[30] present a detailed survey of the determination of boron in graphite, calcium and uranium salts, down to concentration limits of under 0.05 γ per 25 ml. This work, with that of Trego and Silverman[9] (who used curcumin) illustrates the direct application of the technique to the determination of boron concentrations in nuclear fuels.

In our laboratories, we have been using the spectrophotometric method for estimation of boron in uranium compounds using carmine, and in the present paper, we illustrate the points complementary to the work of the authors mentioned,[30] according to our own experience, for the purpose of making the method as efficient as possible, and for clearing up the abnormal points observed in its application.

EXPERIMENTAL PART

Reagents

Included were: boron-free U_3O_8; carmine, Michrome Brand, Edward Gurr Ltd.; carmine 40, R.A.L. special for histology; carmine (lustrous flakes) Merck, p.a.; carminic acid, National Aniline Division, N.Y.; calcium hydroxide, saturated solution prepared from nuclear purity calcium Degussa (kept in polyethylene flasks); sulfuric acid A. R. Probus, 98.9% determined by earlier estimation; perhydrol Merck p.a.; and carmine solution 0.05% (0.92 gm carmine in 1.000 ml H_2SO_4 98.9%).

Equipment

Model DU Beckman Spectrophotometer and Corex cell, 1 cm windows, with plugs was used. Crucibles and evaporating dishes were of platinum or quartz. Automatic burettes were used.

CARMINE-BORIC ACID COMPLEX

For the purpose of studying the influence of carmine of different origins, various products were selected.

With the Edward Gurr, Merck, and R.A.L. carmine, use was made of 0.05% solutions in concentrated sulfuric acid A. R. Probus 98.9%.

For the carminic acid of the National Aniline Division N. Y., the concentration used was such that the transmission measured against distilled water was identical with that of the Edward Gurr carmine.

The measurements were carried out at wavelengths between 540 mμ and 800 mμ, the samples being prepared as follows:

1. A solution which contained 20 γ of boron, and 2 ml of a saturated solution of calcium hydroxide, was evaporated to dryness in a quartz crucible.
2. Exactly 10 ml of the carmine solution was placed in a graduated 25 ml flask.
3. The boron contained in the quartz crucible was transferred to this graduated flask, dissolving the residue of evaporation in concentrated sulfuric acid, and making up to 25 ml.

Original language: Spanish.

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The measurements were carried out at the end of 24 hours, in Corex glass cells, 1-cm thick, using a blank prepared under the same conditions, but without boron.

The values obtained are summed up in Table I.

From Table I, we can see that the boric acid-carmine complex has a maximum optical density between 590 and 625 mμ. 620 mμ was chosen for the working wavelength, in order to reduce interference from possible carbonization of organic substances, the interference of which decreases as the wavelength is increased.

For the purpose of this work, we use the Edward Gurr and R.A.L. carmines, the three types tested being practically identical, while carminic acid is of lower sensitivity.

INFLUENCE OF THE ADDITION OF WATER TO THE RATE OF FORMATION OF THE CARMINE-BORIC COMPLEX AND ITS STABILITY

It was observed that the maximal optical density of the complex formed in a 98.9% sulfuric acid medium was reached after approximately 24 hours for boron concentrations of 1 and 20 γ.

The values are shown in Table II.

A series of tests with varying concentrations of sulfuric acid was carried out, in order to ascertain

Table I. Values of Absorption for Carmines of Different Origins

mμ	O.D. 20γ B Carmine E. Gurr	O.D. 20γ B Carminic Acid	O.D. 20γ B Carmine Merck	O.D. 20γ B Carmine R.A.L.
800	0.000	0.001	0.000	0.000
750	0.000	0.005	0.002	0.003
700	0.019	0.016	0.022	0.022
675	0.116	0.060	0.117	0.120
650	0.393	0.183	0.376	0.367
625	0.532	0.253	0.516	0.510
620	0.535	0.256	0.516	0.510
615	0.535	0.257	0.516	0.510
610	0.535	0.257	0.516	0.510
605	0.534	0.257	0.514	0.508
600	0.535	0.253	0.510	0.508
590	0.534	0.254	0.510	0.500
580	0.492	0.220	0.460	0.466
560	0.412	0.085	0.214	0.306
540	0.390	—	0.050	0.285

Table II

Time	E. Gurr carmine 0.05% O.D. 20 γ boron	R.A.L. carmine 0.05% O.D. 20 γ boron	E. Gurr carmine 0.05% O.D. 1 γ boron
15 min	0.065	0.065	0.004
30 min	0.090	0.090	0.004
1 hr	0.133	0.145	0.007
2 hr	0.210	0.216	—
4 hr	0.305	0.312	—
12 hr	0.468	0.468	—
16 hr	0.495	0.490	0.021
24 hr	0.540	0.510	0.026
26 hr	0.544	0.513	0.026
200 hr	0.569	0.536	0.027

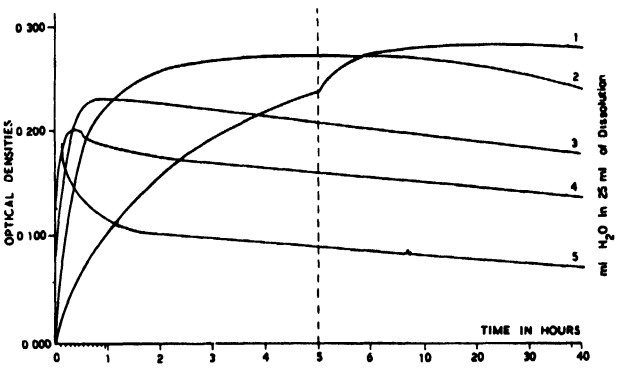

Figure 1. Edward Gurr carmine

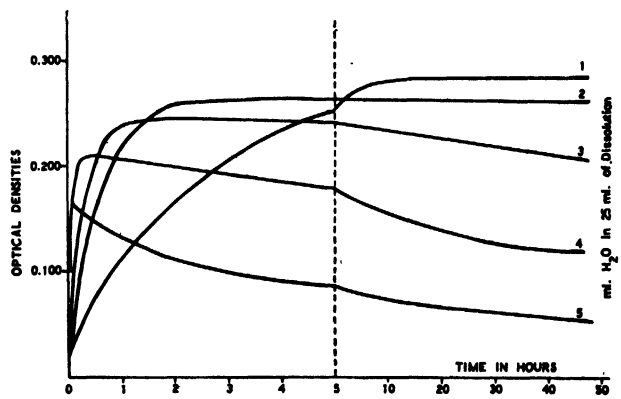

Figure 2. R. A. L. carmine

the possible influence of the acid on the speed of formation of the complex and its stability as a function of time.

One ml portions of an aqueous solution containing 10 γ of boron were placed in 25 ml graduated flasks, followed by water in quantities increasing from 0 to 4 ml, 10 ml of 98.9% sulfuric acid and when cold, 10 ml of the carmine solution, making up to volume with sulfuric acid. The measurements were made at 620 mμ in 1-cm cells using a plug in order to avoid the absorption of humidity.

The results obtained are shown on Figs. 1 and 2.

From these we can see that the rate of formation of the carmine–boric acid complex increases markedly with the amount of water added accompanied by a marked reduction in sensitivity and a smaller stability zone.

When the maximum amount is added, namely 5 ml, the formation of the color is instantaneous, but extremely critical, since it disappears very rapidly and has a sensitivity much smaller than the other values given.

CALIBRATION CURVES

The calibration curves and the determinations were carried out in the manner described for the two methods mentioned: (*a*) using 98.9% sulfuric acid, both to dilute the carmine and to make up to volume, and (*b*) using 93.4% sulfuric acid, which

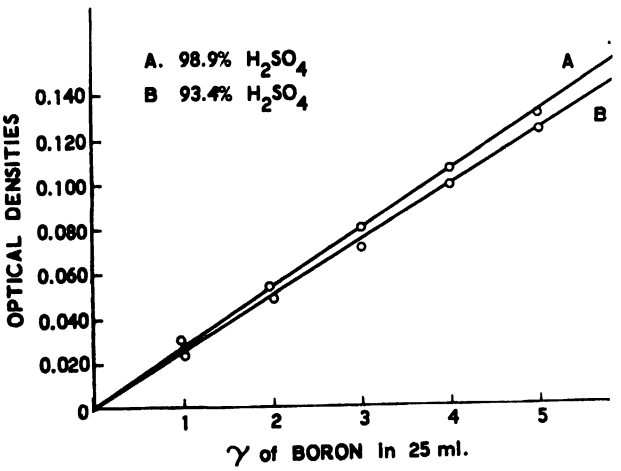

Figure 3. A. 98.9% H_2SO_4; B. 93.4% H_2SO_4

corresponds to the addition of 2.5 ml of water in a final volume of 25 ml (see Fig. 3).

INFLUENCE OF THE NITRATE ION ON THE CARMINE-BORIC ACID COMPLEX

In view of the interest in the determination of boron in uranium nitrate or in compounds from uranium which has been attacked by nitric acid, a series of tests was carried out in order to study the influence of the nitrate ion on the value of the optical density of the carmine-boric acid complex.

Determination in 98.9% Sulfuric Acid Medium

The following were added in succession in quartz crucibles: 2 ml of calcium hydroxide and variable quantities of boron and potassium nitrate. The whole was evaporated to dryness, and the residue dissolved in concentrated sulfuric acid, after which the solution was transferred to 25 ml calibrated containers, in which 10 ml of the 0.05% carmine solution had first been added.

Table III shows the results obtained.

Determinations in 93.4% Sulfuric Acid Medium

In 25 ml calibrated containers we added successively: 1 ml of boric acid solution (equivalent to 10 γ of boron), 1 ml of a solution containing variable amounts of potassium nitrate, 0.5 ml of distilled water, 10 ml of 98.9% concentrated sulfuric acid. When cold, 10 ml of a 0.05 carmine solution were added, thereafter filling up with sulfuric acid (98.9%).

The results are shown on Table III.

From the data shown in Table III, the following conclusions can be drawn:

If the sample to be analysed does not contain boron, the presence of 200 γ of the NO_3^- ion causes no serious interference when dealing with the 98.9% sulfuric medium, or of 500 γ, in the case of the 93.4% medium. Larger quantities give a blue coloration which is equivalent to large amounts of boron.

When there is boron present, the nitrate ion strongly discolors the carmine-boric acid complex formed, mostly in the 98.9% sulfuric acid medium. Quantities as small as 1 γ of nitrate readily bring about considerable loss of color, equivalent to 1 γ of boron. In a 93.4% sulfuric acid medium, the discoloration is smaller.

Adding hydrochloric acid is effective when dealing with determinations in a 93.4% acid medium, making it possible to eliminate interference of up to 1500 γ of nitrate ion, the effect being smaller when the sulfuric acid concentration used is 98.9%.

Table III. Influence of the Nitrate Ion on the Carmine-Boric Acid Complex

γ of boron added	NO_3^- added	Concentrated HCl (drops added)	Boron recovered
Sulfuric acid concentration 98.9%			
10	0.5	—	9.95 ± 0.05
10	1	—	9.00 ± 0.00
10	5	—	8.35 ± 0.35
10	10	—	7.00 ± 0.0
10	20	—	6.45 ± 1.25
10	50	—	7.20 ± 1.50
—	50	—	−0.12 ± 0.0
—	100	—	−0.30 ± 0.02
10	100	—	5.9 ± 0.10
10	100	2	5.3 ± 0.30
—	200	—	−0.60 ± 0.0
10	500	—	3.75 ± 0.25
10	500	2	3.0 ± 0.5
—	500	—	−1.08 ±
10	1000	2	−1.21 ± 0.07
—	1000	—	8.0 ± 0.1
—	1000	2	−0.92 ± 0.20
Sulfuric acid concentration 93.4%			
10	50	—	9.8 ± 0.1
—	50	—	−0.23 ± 0.02
—	100	—	−0.30 ± 0.05
10	500	—	7.65 ± 0.15
10	500	2	9.60 ± 0.05
—	500	—	−0.30 ± 0.05
10	1000	—	7.0 ± 1.0
—	1500	—	30.5 ± 0.5
—	1500	2	−0.18 ± 0.02
10	1500	—	9.75 ± 0.13
—	5000	4	−2.13 ± 0.13
10	5000	4	6.5 ± 0.0
—	10,000	4	−2.70 ± 0.20
10	10,000	4	5.40 ± 0.1

Table IV

U_3O_8	Boron added	Boron recovered	Average value
	98.9% sulfuric acid*		
1 gm	1	0.84	0.91 ± 0.07‡
1 gm	1	0.99	
	93.4% sulfuric acid†		
1 gm	1.00	1.00	
1 gm	1.00	0.85	
1 gm	1.00	1.00	0.94 ± 0.037‡
1 gm	1.00	0.90	

* Peroxide decomposed by heating.
† In the presence of peroxide.
‡ Average error of the arithmetic mean.

Table V. Action of the Light on the Carmine Boric Acid Complex

Time	O.D. 360 mμ	O.D. 425 mμ	O.D. 490 mμ	O.D. 555 mμ	O.D. 620 mμ	Daylight	Artificial light
0 min	0.009	0.010	0.010	0.010	0.011	0.010	0.010
10 min	0.009	0.025	0.011	0.012	0.012	—	—
30 min	0.0095	0.035	0.012	0.013	0.013	—	—
60 min	0.010	0.037	0.013	0.015	0.013	0.018	0.015
90 min	0.010	0.038	0.013	0.018	0.013	—	—
2 hr	—	—	—	—	—	0.520	0.021
4 hr	—	—	—	—	—	1.870	—

INFLUENCE OF THE URANYL ION ON THE CARMINE-BORIC ACID COMPLEX

Determinations in 98.9% Sulfuric Acid Medium

Samples of 1 gm of U_3O_8 were dissolved in quartz crucibles with 1 ml of 98.9% concentrated sulfuric acid, 6 drops of Merck perhydrol and 2 ml of distilled water. This was carefully treated with SO_3 which was passed through the cold solutions in the 25 ml calibrated flasks to which 10 ml of a 0.05% carmine solution had first been added, and ultimately made up to 25 ml with 98.9% sulfuric acid.

The values found are shown in Table IV.

Determination in 93.4% Sulfuric Acid Medium

Samples of 1 gm of U_3O_8 were dissolved in quartz crucibles with 1 ml of concentrated sulfuric acid, 2.5 ml of distilled water and 6 drops of Merck perhydrol, heating slowly until the U_3O_8 was dissolved. It was observed that, under these conditions, and in view of the measurements made with variable quantities of peroxide, excess peroxide which might remain did not interfere with the determination.

Table IV shows the values obtained.

INFLUENCE OF LIGHT ON THE CARMINE-BORIC ACID COMPLEX

These determinations were carried out in the presence of 1 gm of U_3O_8 dissolved in 98.9% sulfuric acid.

Samples of 10 ml of the 0.05% carmine solution were taken, as well as 10 ml of a uranyl sulfate solution (1 gm U_3O_8), making up to 25 ml with 98.9% sulfuric acid.

In order to study the effect of light of various wavelengths on the carmine-boric acid complex, samples were subjected to the action of monochromatic radiation from a Beckman DU spectrophotometer, using the widest slit in order to obtain a beam of maximum intensity. The samples were kept and measured in sealed Corex cells 1 cm thick.

Similar samples subjected to the action of diffused solar light showed a marked increase in optical density, whereas artificial light had a much less marked influence, as can be deduced from the values shown in Table V, which were obtained by the action of a 40 watt fluorescent tube set at 40 cm from the cell in which the complex was formed. All these measurements were made comparatively to targets made up of the reagents without adding U_3O_8, and the samples kept in darkness while the color developed.

The measurements carried out without the addition of U_3O_8 and subjecting the reagents to the same conditions as the tests previously mentioned gave a constant value for the optical density.

The results are shown in Table V.

CONCLUSIONS

The carmine-boric acid complex shows maximal optical density between 590 and 625 mμ, and the value which is practically independent of the carmine used is greater than that when carminic acid is used.

The rate of formation of the carmine-boric acid complex is markedly affected by the concentration of the solution in water, a factor which also influences the sensitivity and stability figures, which increase as the aqueous concentration decreases.

The optimal working condition chosen (taking into consideration the rate of formation of the carmine-boric acid complex, the stability and the sensitivity of the measurements), is provided by making the measurements in a 93.4% sulfuric acid medium.

Nitrate ions markedly influence the absorption when a 98.9% sulfuric acid medium is used. This effect is much smaller for a concentration of 93.4%. The addition of hydrochloric acid in a 93.4% sulfuric acid medium eliminates interference up to 1500 γ of nitrate ion. This incompatibility is not eliminated in the case of 98.9% sulfuric acid.

Concentrations of 1 gm of U_3O_8 in 25 cm^3 do not affect the determination in the acid media used.

Diffused solar light affects the carmine-boric acid complex and has a considerable effect on the optical density.

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TUESDAY MORNING, 16 AUGUST 1955

Chairman: Mr. H. Brynielsson (Sweden)
Vice-Chairman: Mr. D. W. Seelman-Eggebert (Argentina)
Scientific Secretaries: Messrs. R. Hara and B. Prakash

PROGRAMME

P/952	Analysis of uranium and thorium raw materials	C. J. Rodden
P/627	Physico-chemical methods of uranium production control	A. P. Vinogradov
P/942	Contributions to methods of measuring the concentrations of uranium and thorium in minerals (nuclear emulsions)	A. Soltan
P/964	Polarography of uranium: Polarographic determination of uranium in ores without preliminary chemical separation	M. V. Susić
P/630	The physical method of determining the content of uranium, radium and thorium in radioactive ores	G. R. Golbek *et al.*
P/1008	Determination of the U^{235} content of uranium by a radiochemical method	I. G. de Fraenz and W. Seelman-Eggebert

DISCUSSION

Mr. C. J. RODDEN (USA) presented paper P/952.

Mr. A. P. VINOGRADOV (USSR) presented paper P/627 as follows:

Where the production of uranium is concerned, research workers have been faced with two basic problems: developing methods of quality control for every stage of the refining process from the raw ore to the uranium rod, and evolving analytical procedures to determine the content of impurities, particularly neutron-active admixtures, in the metal.

As a rule, the methods we developed were based on the following distinctive properties of uranium: radioactivity, ability to luminesce in solutions and in solid beads and, lastly, ability to be extracted into many non-aqueous solvents in the form of uranyl ions.

All these properties were made use of in devising the many and divers chemical and physico-chemical methods which we employed (some of these have been described in our other papers, P/628 and P/629). Although they are very accurate, chemical methods are very time-consuming.

Combination of chemical preparation of specimens of uranium ore and rock and intermediate products (i.e., concentration and other forms of enrichment) with instrumental methods (spectroscopy, radiometry, luminescence, polarography, etc.) leads to better results as regards reproducibility and appreciably reduces the time required for analysis.

Even better results in this sense can be obtained by using certain instrumental methods for direct determination of the uranium or of the impurities without prior chemical preparation.

These methods require the least time and come nearest to universal methods of analysis. They are now widely employed in quality control of uranium production in our country.

However, even in my printed report I did not have space to describe most of them and could only record the results we have achieved in the fields of emission spectroscopy for determining uranium and impurities in it, spectrographic determination with the addition of light isotopes of uranium, X-ray spectrum analysis for impurities in the uranium (particularly rare earths), polarography and oscillographic polarography. The method of radiometric determination of uranium in ore and rock is partially explained in document P/630 and the radioactivation method in our other paper, P/632.

In my present brief statement I shall have to confine myself to a still more limited number of questions. I want to draw attention to some relatively new physico-chemical methods for the direct determination of uranium and its impurities—i.e, to the determination of the admixtures in refined uranium by emission spectroscopy, isotopic analysis of uranium in ores and semi-refined uranium, and oscillographic polarography of uranium ore and the impurities present in it. I believe that these methods are promising and may prove useful not only in quality control in uranium production but also in the refining of other metals. They are, in my opinion, worthy of our consideration.

Any method used for determining impurities in metallic uranium or its oxide, particularly neutron active impurities such as Li, B, Be, Cd, and Te, must have a sensitivity of not less than 10^{-5}% and great accuracy. The difficulty in working out a spectroscopic method for this purpose stemmed from the fact that the spectrum of uranium comprises a large number of relatively weak lines spread over a very intense continuum. Hence, it is necessary first to separate the uranium from the impurities. We succeeded in doing this by the evaporation of the impurities from U_3O_8 at 2000°C. As we know, Scribner and Mullin also evaporated the impurities (with carriers) and excited the spectrum of the evaporating impurities. We chose a different course.

The process of evaporating the impurities was separated from the process of exciting the spectra of these impurities, by having the impurities condense on electrodes.

It was shown by spectrum and chemcial analysis, using tagged atoms, that virtually complete evaporation and subsequent condensation of the impurities on the electrodes is obtained. This means that the sensitivity of the analysis can be greatly increased by accumulating the material.

At the same time, condensation of impurities on the surface of the electrodes—for example, graphite electrodes—made it feasible to lower the requirements as regards electrode purity. This is an important consideration, since the preparation of very pure electrodes is a difficult matter. We also showed that the method of evaporation does not require carriers.

It proved possible under plant conditions to make consistent determinations of impurities in the uranium in amounts of 1 part in 10^6–10^7, with an accuracy of 10–15%. Thus, the sensitivity of the method is very high. The data I cited in my printed report comparing this evaporation method with the method of exciting the spectra of the evaporating impurities, without preliminary condensation, show the merits of the method we have evolved.

It is known, however, that the intensity of the spectral lines of the elements present in the specimen depends strongly on the over-all chemical composition of the specimen. This limits the range of application of spectroscopic methods of analysis and often makes them unsuitable for analysis of substances of varying over-all composition. Hence it is always necessary to consider the possible influence of extraneous, interfering elements in the specimen.

An effective method of reducing this influence on the analytical results to a minimum, and enhancing the accuracy and universal applicability of the spectroscopic method is to use isotopes of the element in question as an internal standard. Under these conditions, the relative intensity of both "isotopic components" of the spectral lines of this element will be virtually independent of the conditions of evaporation and excitation of the element and will be determined primarily by the relative concentration of the isotopes in the specimen.

In investigating the spectrum of uranium we discovered many lines with isotopic shifts. We decided that the 4244Å line was most suitable to work with.

U^{235} and U^{233} were used as internal standards. We developed and applied a method for determining uranium in various ores, minerals and concentrates, having uranium contents ranging from 0.01 to 5% and higher. With this method, the specimen requires no chemical preparation beyond mixing with the light uranium isotope. Complete analysis requires 1 to 2 hours. We attained an accuracy of within 2.5%. Table I shows the results of a series of determinations of uranium in different materials, obtained in a refining plant. Only 1 mg of uranium-235 or uranium-233 is required for 250 determinations.

A limit on greater accuracy is imposed by the characteristics of the photographic emulsions. It should be possible to increase the accuracy to within 0.5%, but photo-electric detection would have to be used instead of plates.

We were able to compare and evaluate the method of isotope addition in connexion with both spectroscopic and mass-spectroscopic determination. In mass-spectroscopy, the uranium must be separated from the specimen, which takes an appreciable amount of time. Moreover, the mass-spectroscopy procedure is rather difficult and consumes a great deal of time. However, an accuracy of within 1% or less may be attained. In practice, the spectroscopic method (with the addition of U^{235} or U^{233}) proved more advantageous. It is nearly as accurate as chemical methods of analysis and is much more rapid.

Lastly, I would like to say a few words regarding oscillographic polarography as applied in quality control of uranium production.

In oscillographic polarography, a saw-tooth voltage proportional to that applied to the polarographic cell is applied to the horizontal deflection plates of the cathode-ray tube, while a voltage proportional to the current flowing through the cell is applied to the vertical deflection plates. Thus, a voltage-current curve is obtained on the oscillograph screen. In certain cases the wave-height is proportional to the concentration of the reducing agent.

Slide 1 (Fig. 7 of P/627) shows a typical saw-tooth oscillogram. The beginning of the sharp increase in current depends on the nature of the material analyzed, i.e., its reduction potential. The maximum current value corresponds to the concentration of the substance in the solution.

We investigated the mechanism of the reduction of the uranyl ion UO_2^{2+} and established the conditions necessary for determining a number of simultaneously present impurities. Two uranium waves occurring in different media were discovered.

The first uranium wave, corresponding to the $UO_2^{2+} + e \rightleftarrows UO_2^{+}$ transition, is shown in Slide 2 (Fig. 8 of P/627), while the second wave, corresponding to the $UO_2^{+} + 2e \rightleftarrows U^{4+}$ transition, is

Table I

The average according to spectral analyses, %	*Deviation from the average, %*	*The average according to chemical analyses, %*	*Difference between spectral analyses and chemical analyses, %*
2.13	3.0	2.14	— 0.5
2.03	2.0	1.99	+ 2.0
2.13	3.0	2.02	+ 5.0
1.70	2.0	1.68	+ 1.2
2.02	1.5	1.98	+ 2.0
2.22	5.0	2.24	— 1.0
2.29	0.4	2.26	+ 1.3
2.44	3.0	2.47	— 1.2
2.13	3.0	2.14	— 0.5
1.68	2.2	1.72	— 2.0
2.03	2.0	1.99	+ 2.0
2.13	3.0	2.02	+ 5.0
2.02	1.0	1.97	+ 3.0
1.70	1.2	—	—
2.05	2.0	1.98	+ 3.5
2.09	1.0	2.12	— 1.5
1.75	2.3	1.77	— 1.1
1.92	4.0	1.91	+ 0.5
1.90	4.0	1.91	— 0.5
2.12	6.0	2.30	— 8.0
1.70	0.0	1.79	— 5.0
2.00	0.0	2.13	— 6.0
2.20	1.4	—	—
1.96	2.5	1.97	— 1.0
2.00	0.0	1.95	+ 2.5
1.66	6.0	1.66	0.0
1.80	2.8	1.70	+ 6.0
1.71	4.0	1.72	— 0.6
1.71	3.6	1.71	0.0
2.03	2.0	2.07	2.0

shown in Slide 3 (Fig. 10 of P/627). A third wave proved to be due to traces of zinc.

In practice it proved possible, for example, to determine simultaneously lead and other ions present in appreciable concentrations in the uranium solution. The determination of lead is highly important in establishing the absolute geological age of a mineral formation. An example of such a simultaneous determination of lead and uranium is shown in Slide 4 (Fig. 9 of P/627). The uranium and lead waves may be seen in the figure.

One of the merits of the method of oscillographic polarography is that it is 1–1.5 orders of magnitude more sensitive than that of ordinary polarography. It permits us to distinguish between ions whose reduction potentials differ only slightly.

Mr. A. SOLTAN (Poland) presented paper P/942 as follows:

I would like to present a brief report on the research carried out by the late Mr. Pienkowsky and some of his collaborators on the distribution of uranium and thorium deposits in Poland.

These investigations are concerned with problems of geology and petrography. I nevertheless thought it worth while to report on them here, as they may throw some light on how these two elements, which are of such importance in nuclear physics, are amassed in the earth's crust. Being a physicist myself, I can only describe the experimental method used and the results obtained, without going into mineralogical and geo-chemical explanations.

The investigation was pursued along two different lines and was aimed at: (1) studying crystal inclusions associated with uranium and thorium, and (2) measuring the average concentration of these elements in larger volumes of rock formations.

The first involves the examination of a highly polished section of the mineral in question, both in view of the nature of the inclusions and in view of the number of alpha particles emitted by different faces per unit surface and time. As the inclusions are usually very small, the following method was adopted: plates were cut from the mineral formation investigated and were reduced by grinding and polishing to a thickness of about 30 microns. Liquid nuclear photographic emulsion was applied to the stone plates. After drying, the emulsion adhered to the plate and recorded the alpha particles emitted by the specimen till the time of development. A transparent support was obtained for the specimen which permitted studying its structure and provided a way for simultaneously recording the alpha particle emission at every point. Thus by microscopic examination of the emulsion and the specimen it was possible to establish a close correlation between the character of the inclusions and their radioactivity.

In addition to confirming the already known fact that uranium and thorium are associated with inclusions of zircon in biotite, the investigators made a new discovery; namely, that uranium alone, without thorium, is found in very much larger amounts in iron oxide inclusions.

Investigations of the average concentration of uranium in larger volumes of uranium-bearing minerals were carried out on specimens reduced to a powder The uranium and thorium content was measured either by means of Geiger-Müller counters or with the aid of nuclear emulsions. These methods, as well as the corrections which must be made in the readings, are to well known to need description here.

Among what I consider to be the most interesting results of the research are those establishing a correlation between the uranium content of phosphorites and the age of the geological formation from which the specimen was taken. This correlation is illustrated by a table and a graph which are to be found in our paper. The numbers in the table show that radioactivity in the phosphorites examined varied from specimen to specimen. This radioactivity varies monotonously with the age of the formation, decreasing in a ratio of 40 to 1 as the age increases from 80 to 400 million years.

An interesting fact is that some specimens with a radioactivity of about 4%—in other words, the same degree of radioactivity—were taken from geological formations very close to each other in age but over 200 kilometres apart. The existence of such a relation between the radioactive substance content and the age of the phosphorites strikes me as very interesting. It may be due to the conditions which pre-

vailed when the deposit was formed or to its subsequent evolution. However, it would be premature to draw any definite conclusions on that score. The research in progress will undoubtedly bring to light new facts.

Mr. M. V. Susić (Yugoslavia): presented paper P/964 as follows:

The ascorbic supporting electrolyte for the polarographic determination of uranium deserves special attention. Its reducing and complex-forming capacities permit the determination of uranium in the presence of a considerable excess of other elements and also in ores, without preliminary separation.

Studying the uranium wave in ascorbic supporting electrolyte in the pH range from 1–9.5, it was found that at pH < 2 the wave possesses a certain residual current—for the uranium concentrations below 10^{-5} gm/ml. An increase of pH produces a decrease of the residual current which disappears at pH < 3.5.

By measuring the diffusion current at different pH, and different known concentrations of uranium, it was found that the ratio between the diffusion current and the uranium concentration is constant, that is $id/e = k$ in the pH range from 1–9.5. This shows that uranium can be determined either in acid or in alkaline media with ascorbic supporting electrolyte. Because of the complete absence of oxygen one obtains a well formed wave for the uranium concentration of 2×10^{-6} gm/ml.

Since the ascorbic acid reduces all ions more positive than 0.5 volts vs hydrogen to a state of lower valency and forms soluble complexes with reduced as well as with non-reduced ions—more negative than 0.5 v with reference to hydrogen—we were able to determine uranium in the presence of a considerable excess of a great number of other elements.

A considerable number of ores of different composition were analysed. The results were compared with those obtained by other methods: colorimetric, fluorimetric and radiochemical. The agreement between the different methods is good.

The method of alkaline ascorbic supporting electrolyte was used to determine uranium in carbonate solutions of ores. Since the ores in most cases contain organic materials which pass into the carbonate solution and interfere with the determination of uranium, they had to be destroyed with nitric and sulphuric acids. The dry residue of sulphates is dissolved in water, ascorbic acid added and then ammonia until the medium becomes alkaline. The solution is then analysed. It was not necessary to bubble the solution with nitrogen, nor to add gelatine. Excellent uranium waves, without interferences, were obtained.

This method is especially convenient for checking the carbonate dissolution of uranium ores, rich in vanadium and molybdenum, on an industrial scale.

The polarographic investigation of the reduction of the uranyl ascorbic complex at the dropping mercury electrode showed that this reduction is reversible and involves the exchange of one electron. A mixture of U(VI) and U(V) complex in the ascorbic supporting electrolyte gives an anodic-cathodic wave having the same half-wave potential.

From the change of the half-wave potentials of the uranyl ascorbic complex, effected by the change of the concentration of the ascorbic supporting electrolyte, we have determined certain constants relating to the electrode reaction.

Mr. L. M. Barkov (USSR) presented paper P/630 and added the following statement to the published text:

Recently the apparatus I described has been somewhat modified: the sensitivity of the gamma-ray coincidence indicators has been doubled by the introduction of a system registering coincidences between neighbouring counters in each annular layer. This two-fold increase in the sensitivity of the equipment has made it possible to reduce the weight of the samples required by half: i.e., to 300 grams.

Mr. I. G. de Fraenz (Argentina) presented paper P/1008.

DISCUSSION OF P/952, P/627, P/942, P/964, P/630 AND P/1008

The Chairman: The first question is on paper P/952 and is addressed to Mr. Rodden. It comes from Mr. A. A. Smales of the United Kingdom: "I would be glad to have the author's opinion on the value of the lead reductor in the colorimetric determination of uranium. It would seem to have the advantage that reduction takes place only to the tetravalent stage, so that you avoid the aeration step."

Mr. Rodden (USA): The lead reductor has been used to a considerable extent by certain people in the United States, and I believe that it has been used more in the low grade ores than in the high grade. We have never tried it in the high grade ores, so that I cannot say. I am sorry I cannot do any better than that.

The Chairman: Now we have some questions addressed to Mr. Vinogradov.

Mr. Vinogradov (USSR): I have been handed a number of questions:

1. Can you describe the equipment for evaporating and collecting the impurities in analysis of uranium for impurities?

Answer: The main part of the equipment is a graphite rod some 2–3 cm in length and 0.6 cm in section, which has a crater 1.5–2 mm across and about 10 mm deep. The U_3O_8 is packed into this crater. Then the graphite rod is placed in a resistance furnace with either a carbon or a water-cooled copper electrode suspended 1–3 mm above it; the distilled impurities condense on this electrode, which is the electrode used to produce the spectrum.

2. If the time required to evaporate this specimen is two minutes, what other operations account for the analysis time?

Answer: At the plant, in the case of spectral determination, results are obtained in about 15 minutes,

but when the spectrum must first be photographed much more time is required. We use a number of different spectroscopes for the impurity determinations; these are all medium dispersion instruments. Our spectroscope is very similar to the Hilger No. 24 spectroscope. This spectroscope can be used for determining the impurities in uranium. Determinations by the method of isotopic additions require a spectroscope with a higher dispersion; our spectroscope has a dispersion of 2Å per mm.

3. In determining uranium by the X-ray method do you use fluorescence instruments or do you do this by means of a target?

Answer: In the case of determining rare earths in uranium we carry out the analysis with reference to a standard. But we also use more complex analytical procedures. They have all been described; in connexion with this I would like to call your attention to the references by Vainshtein *et al.* cited in my written report, where both theoretical and practical aspects of the problem are discussed in detail.

4. Is the concentration process necessary in determining rare earths in uranium?

Answer: Calculation readily supplies an answer to this question. About 10^{-7} grams of the rare earths is required for X-ray spectrum analysis. Usually these are present in uranium in the amount of 10^{-6}%. Consequently many-fold enrichment is necessary. Complete elimination of the uranium is desirable but not absolutely necessary.

5. How much time does the chemical part of the procedure require?

Answer: It requires as much as a full working day; the photography itself of course is quickly accomplished. We are currently using three different methods for determining rare-earth elements in uranium: X-ray spectrum and emission spectrum analysis and radioactivity analysis. The composition of the mixture of rare earths can be successfully determined by any one of these methods.

The CHAIRMAN: There are three more questions for Mr. Vinogradov from Mr. Smales of the United Kingdom. First: In the enhancement of the uranium polarographic step by vanadium, could Professor Vinogradov suggest by what mechanism this takes place? Could vanadium be used in a fixed amount in the base electrolyte to give increased sensitivity for uranium?

Mr. VINOGRADOV (USSR): We know that vanadium always interferes with determination of uranium by polarographic as well as other methods. A vanadate-uranyl complex is formed in the presence of vanadium. This has been discussed in one of our reports. However, in this case the sensitivity of the polarographic determination of uranium is increased.

The CHAIRMAN: The next question is: In the internal standard method for optical spectrographic determination of uranium, how is the trace of uranium introduced, and what increased complexity from the health hazard point of view is involved in its use?—in the international standard perhaps.

Mr. VINOGRADOV (USSR): Working with uranium under laboratory conditions presents no hazard. Usually one must have a standard containing U^{235}. When it is necessary to introduce U^{235} it is mixed with some suitable neutral medium and then the mixture containing the diluted isotope is added to the sample being analysed for uranium.

The CHAIRMAN: The third question is: If a chemical separation of rare earths is necessary before X-ray spectrographic examination, is there any advantage in using the latter technique over that of optical spectroscopy?

Mr. VINOGRADOV (USSR): In both cases the rare earths have to be separated from the uranium. But spectral analysis in the presence of a number of extraneous elements accompanying the rare earths does not give accurate results. The accuracy in spectral analysis is within 50–100% while X-ray spectral analysis gives an accuracy of within 5–10% for a mixture of rare earths. The choice of technique will depend on the purpose of the analysis.

The CHAIRMAN: Thank you very much for those answers, Mr. Vinogradov. Now there is a question from Mr. Rodden (USA) to Mr. Soltan: "How do you differentiate between thorium and uranium in rocks which contain both elements, and how is the age of the minerals cited determined?"

Mr. A. SOLTAN (Poland): From observation of the stars one can tell whether the scintillation is due to uranium or thorium. The path lengths of the alpha-particles are also known. Consequently, using the methods recently developed by Mrs. Joliot-Curie and others, one can determine the relative concentrations of thorium and uranium.

The second question was: How is the age of the deposit determined? This is done by geologists. The age is known within an approximation of 10 to 20%.

The CHAIRMAN: We have a question here from Mr. Rodden to Mr. Susić: "What are the effects of vanadium and molybdenum when you analyze uranium containing mixtures of these elements?"

Mr. SUSIĆ (Yugoslavia): They do not give in an electrolytic media any waves, and in an acid, vanadium less than in equal amounts does not disturb at all; nor does molybdenum if it is more than 3 times the uranium concentration.

The CHAIRMAN: Now we have two questions on P/630 to Mr. Barkov. The first one is from Mr. G. N. Walton (UK): "I should like to ask the author of paper P/630 if the density or degree of porosity of the specimen is allowed for in the estimation? Beta rays are absorbed more readily than gamma rays and this would be expected to affect very appreciably the conclusions drawn."

Mr. BARKOV (USSR): Variations of the specimen density introduce very little error into the measurement of the total gamma radiation and of the hard gamma radiation since the gamma counter is shielded by a layer of lead 1.5 mm thick, and

consequently self-absorption of the specimen has little effect on the measurements. In the case of the beta counter we introduce the necessary corrections for the density of the specimen. This applies to the case of very dense specimens. Moreover, self-shielding where the beta counters are concerned has little apparent effect by virtue of the fact that this counter is not particularly sensitive to soft gamma radiation.

The CHAIRMAN: There is finally a question here from Mr. Rodden: "After sealing the sample in the aluminum cylinder, how long do you have to wait before making measurements? Do you have to wait until equilibrium with the radium is reached? How do you seal the cylinder to prevent leakage of radon?"

Mr. BARKOV: (USSR): Leakage of radon from the specimen is prevented in the following manner. A rubber gasket is provided between the container holding the specimen and the cover which screws on to the cylinder; this gasket ensures a tight seal and prevents leakage of radon. In our measurements we usually did not wait until equilibrium between the radium and radon was established. Usually this occurs after the cylinder has been sealed, for it takes several hours for the radium decay products to reach equilibrium with the radon. In cases when it is desired to know the radium content another measurement is made several days after the first one. Then the amount of radium in the ore can be evaluated from the increase in the count rate.

Session 16B.1

PRODUCTION TECHNOLOGY OF SPECIAL MATERIALS: HEAVY WATER

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Survey of Heavy-Water Production Processes

By Manson Benedict,* USA

1. INTRODUCTION

This paper describes those processes for the production of deuterium or heavy water which have been used on an industrial scale or which appear to have economic merit.

Attention is devoted to the principle of each process, the physical factors on which separation depends, the general type and arrangement of equipment leading to minimum cost, and, where information is available, the probable cost of heavy water made in an efficient plant. Where relevant to these topics brief descriptions are given of processes developed in the United States and those described by European workers, but, no attempt is made to present a complete history of the heavy water industry. A detailed account of heavy-water developments under the Manhattan District in the United States is given by Maloney and Ray.[16]

Because of the low proportion of deuterium to hydrogen in nature (140 to 150 part per million) and the large amount of heavy water needed per reactor (5 to 200 tons) an economically feasible process for separating deuterium must be capable of handling large amounts of material at low unit cost. Although the difference in properties between a compound of hydrogen and the corresponding compound of deuterium is comparatively large (for isotopes), and many processes have been discovered which separate these isotypes on a small scale, only a few will do so economically on a large scale. The separation methods which appear to be best suited for large scale production are (1) distillation, (2) electrolysis of water, and (3) chemical exchange. Discussion will be confined to these methods.

Separation methods excluded from discussion because of anticipated high costs for energy, chemicals or material handling, or because of excessive working inventory of partially enriched deuterium, include:

1. Processes involving movement or batch handling of solids, such as adsorption or ion exchange.
2. Processes using only condensed phases, such as solvent extraction or fractional crystallization.
3. Processes dependent on differences in reaction rates of isotopic substances.
4. Processes dependent on differences in diffusion rates, such as diffusion through a porous membrane, thermal diffusion, or differential ion migration.

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1.1 Distillation

For separation by distillation to be economic it is necessary that the vapor pressure of a compound of hydrogen differ significantly from that of the corresponding compound of deuterium. Table I gives the ratio of the vapor pressures of several common compounds of hydrogen to the corresponding compounds of deuterium, at the triple point temperature and at the normal boiling temperature of the hydrogen compound. For each compound, the vapor pressure ratio is most favorable at the triple point, the lowest pressure at which distillation is possible.

Hydrogen is the only one of these substances which has a vapor pressure ratio as favorable as in conventional industrial distillation. In this case, however, the relative volatility for isotope separation is less favorable than the tabulated vapor pressure ratios because of non-idealities in gaseous and liquid mixtures of hydrogen and HD. Moreover, it is desirable to operate above atmospheric pressure, to preclude inleakage of air. Under practical conditions, at 1.6 atm, the relative volatility obtainable is around 1.40.

With water it has been shown experimentally[13] that the relative volatility for isotope separation at 100°C is equal to the square root of the ratio of the vapor pressure of H_2O to D_2O, the quantity tabulated. This is true when:

1. The vapor pressure ratio of H_2O to HDO is the same as HDO to D_2O.
2. The distribution of deuterium and hydrogen atoms at equilibrium in the liquid phase among H_2O, HDO and D_2O is random.
3. Gaseous and liquid mixtures of these compounds form ideal solutions.

For ammonia it is assumed that similar conditions hold, so that the relative volatility for isotope separation equals the cube root of the ratio of vapor pressure of NH_3 to ND_3.

Methane cannot be used as working substance in a distillation process because its relative volatility is so close to unity. This is regrettable because of the large amount of natural gas which might be used as a source of deuterium.

Although water has a slightly less favorable relative volatility than ammonia, water makes the better working substance because it can be distilled at ordinary temperatures, whereas ammonia requires refrigeration and special construction materials.

Table I. Vapor Pressure Ratios of Isotopic Compounds of Hydrogen

Ratio of	Vapor pressure ratio at		Triple point		N.B. pt. °C	Reference
	Triple pt.	N.B. pt.	P, mm	t, °C		
o-H_2/HD	3.61	1.81	54	− 259.4	− 252.9	27
$\sqrt{NH_3/ND_3}$	1.080	1.036	45.6	− 77.7	− 33.6	15
$\sqrt{H_2O/D_2O}$	1.120	1.026	4.6	0.0	100.0	13
CH_4/CH_3D	1.0016	0.9965	87.5	− 182.5	− 161.9	1

Water is available in unlimited quantities, whereas the amount of deuterium which could be extracted from ammonia is limited to the amount present in ammonia produced industrially.

Hydrogen, with by far the most favorable relative volatility, should make the best working substance for a distillation plant, although the need to operate at unconventionally low temperatures and the limitation in output set by the amount of deuterium present in hydrogen produced for industry are disadvantages.

1.2 Chemical Exchange

Separation by chemical exchange makes use of reactions of the type of

$$H_2O + HD \rightleftharpoons HDO + H_2$$

in which the ratio of deuterium to hydrogen at equilibrium in one pair of isotopic compounds (H_2O + HDO) differs from the ratio in the other pair (H_2 + HD). When these two pairs of compounds are moved countercurrent to each other in different phases, separation of deuterium from hydrogen may be effected in a manner similar to separation of different chemical species by gas-liquid absorption or liquid-liquid extraction.

Equilibrium constants for deuterium exchange reactions are listed in Table XIII of Section 7, where it is shown that the most suitable reactions are

$$H_2O + HD \rightleftharpoons HDO + H_2 \ (K = 2.69 \text{ at } 100°C)$$
$$H_2O + HDS \rightleftharpoons HDO + H_2S \ (K = 1.92 \text{ at } 100°)$$
$$NH_3 + HD \rightleftharpoons NH_2D + H_2 \ (K = 5.83 \text{ at } 25°C)$$

Reflux for the countercurrent exchange contactor may be obtained in one of two ways: (1) in simple chemical exchange, by chemical conversion of one deuterium-rich compound to the other (e.g., HDO to HD), or (2) in the "dual-temperature" process, by a second exchange contactor operated at a different temperature than the first, with a different equilibrium constant.

The chemical conversion used in the simple exchange process is costly, and would not be used unless the conversion product is valuable and marketable. Of the three reactions listed above, only the conversion of water to hydrogen is profitable; conversion of ammonia to hydrogen is an economic loss, and conversion of water to hydrogen sulfide cannot be exploited on the scale necessary in a heavy-water plant. Thus, only the steam-hydrogen reaction is useful in the simple exchange process; all three reactions may be considered in the dual-temperature scheme.

1.3 Processes Considered

For the reasons sketched above, the following processes are to be considered in this paper: Section 2, distillation of hydrogen; Section 3, distillation of hydrogen, combined with steam-hydrogen exchange; Section 4, distillation of water; Section 5, electrolysis of water; Section 6, simple steam-hydrogen exchange process; and Section 7, dual-temperature processes. In Section 8, the processes are compared and conclusions are drawn regarding their usefulness and cost.

2. DISTILLATION OF HYDROGEN

2.1 History

The samples of hydrogen enriched in deuterium in which Urey, Brickwedde and Murphy discovered this isotope in 1932[25] were prepared by the fractional evaporation of liquid hydrogen Despite this early indication of the utility of this process, it has not yet been used commercially, primarily, because of the lack of industrial experience with large plants operating at liquid hydrogen temperatures.

Production of deuterium by the distillation of hydrogen was given serious consideration by the Manhattan District in the United States. In 1943, preliminary plant designs and cost estimates were developed by engineers of the duPont Company working in collaboration with Urey.[16] This work showed that the distillation of hydrogen was a more economical process for producing deuterium than other methods then available. Nevertheless, work on this process was stopped and plants using the steam-hydrogen exchange reaction and the water distillation process were built instead. The decision not to use the low-temperature process at that time was primarily a result of uncertainty regarding the length of time required to solve the novel engineering problems connected with handling large quantities of gases at low temperature.

Studies in Germany carried out at about the same time by Clusius and Starke[5] also showed the promise latent in this process. With the aid of engineers of the German Linde Company, process designs for a hydrogen distillation plant were worked out. Clusius and Starke concluded that deuterium could be produced by the distillation of pure liquid hydrogen with a power consumption of only 4.8 kilowatt hours per gram of heavy water, whereas electrolysis required from 120 to 150 kilowatt hours

per gram. These workers conducted the first experimental work on the fractional distillation of liquid hydrogen and showed that a mixture of hydrogen, HD and deuterium could be separated by fractional distillation at atmospheric pressure into relatively pure fractions of H_2, HD, and D_2 without HD undergoing disproportionation and without appreciable conversion of ortho to para modifications.

Based on this experimental work, the distillation flowsheet shown in Fig. 1 was proposed by these authors. Natural hydrogen containing 0.028% HD at slightly above atmospheric pressure is cooled to its dew point (around —420°F) and fed into the primary distillation tower. In this tower it is fractionated into an overhead product substantially free of HD and a bottoms product containing from 5% to 10% HD. The bottoms from this tower are fed into the upper half of a smaller secondary tower, where fractionation into a bottoms product of nearly pure HD is completed. This HD is warmed

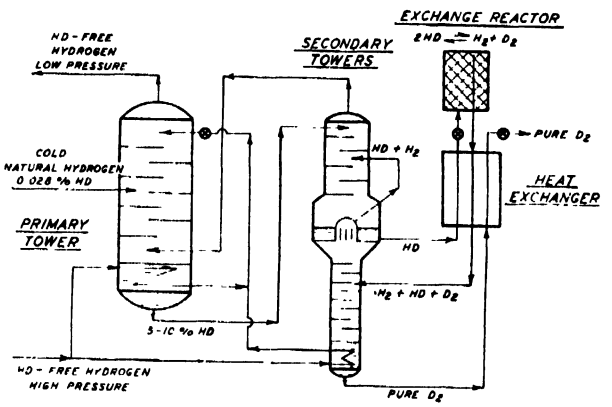

Figure 1. Flowsheet for production of deuterium by distillation of liquid hydrogen (Clusius and Starke)

to room temperature in a heat exchanger and passed through a catalytic exchange reactor where its disproportionation into an equilibrium mixture of H_2, HD and D_2 is catalyzed. The product of the exchange reaction is cooled to liquid hydrogen temperatures in the heat exchanger and fed to the bottom half of the secondary tower where it is fractionated into an overhead product of HD + H_2 and a bottoms product of pure deuterium. This is warmed to room temperature in the heat exchanger and constitutes the product of the plant. The HD and H_2 overhead from the bottom of the secondary tower is fed to the top of the secondary tower for recovery of HD.

Heat to reboil these towers is provided by a stream of compressed, HD-free hydrogen, which is condensed in reboiler coils located in the sump of these towers. The condensed HD-free hydrogen is then used as open reflux in the top of the primary tower. A Linde, double-column arrangement is used to provide reflux for the bottom of the secondary tower and reboil vapor for the top of this tower.

In 1950 and 1951 this process was carried one stage further towards industrial realization when Hydrocarbon Research, Inc. was authorized by the US Atomic Energy Commission to design a plant to produce deuterium by distillation of liquid hydrogen obtained from synthesis gas at one of the synthetic ammonia plants in the United States. An experimental program to provide data necessary for this design was carried out and the design itself was nearly completed. The plant, however, was not built. This work has been described in report NYO-889 of the US Atomic Energy Commission.[12] A brief description of the process and plant designed by Hydrocarbon Research and some of the design problems encountered is given in the following sections of this article. The main reason for the decision not to build this plant was again lack of experience in handling liquid hydrogen on so large a scale.

It has recently been announced that the French Atomic Energy Commission has authorized Société de L'Air Liquide to design and build a plant for the production of deuterium by the distillation of liquid hydrogen obtained from synthesis gas at the ammonia plant of Société de L'Air Liquide at Toulouse, France. This will be the first reported commercial application of this process.

2.2 Hydrogen Distillation Process of Hydrocarbon Research, Inc.

2.21 Plant Location and Specifications

It is not economical to produce hydrogen solely for the purpose of extracting deuterium. Hydrogen produced commercially, as by reforming natural gas, costs around 50¢ per thousand cubic feet; this corresponds to around $75 per pound of heavy water. A hydrogen-distillation deuterium plant is therefore necessarily parasitic, taking a stream of hydrogen-rich gas produced for other purposes, extracting most of the deuterium, and returning the deuterium-free hydrogen to the host plant.

In 1949–1950 Hydrocarbon Research, Inc. conducted a survey of large sources of gases rich in hydrogen in the United States, and concluded that the largest synthetic ammonia plants then in the U.S.A. were suitable sources of hydrogen for separation of deuterium by distillation.

For low-cost deuterium production, the production rate of ammonia should be at least 300 tons per day. Coke-oven gas was recognized as another possible source of hydrogen, but a less suitable one because of the greater cost of purification.

It was found that hydrogen in synthesis gas of these ammonia plants contained from 108 to 127 parts per million of deuterium instead of the normal 149. This low value was traced to the water-gas shift reaction used to make hydrogen

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

in which deuterium tends to concentrate in unconverted steam, which was not being recycled. It was believed that most of this steam could be recovered and reused, to bring the deuterium content up to 136 parts per million. At this feed concentra-

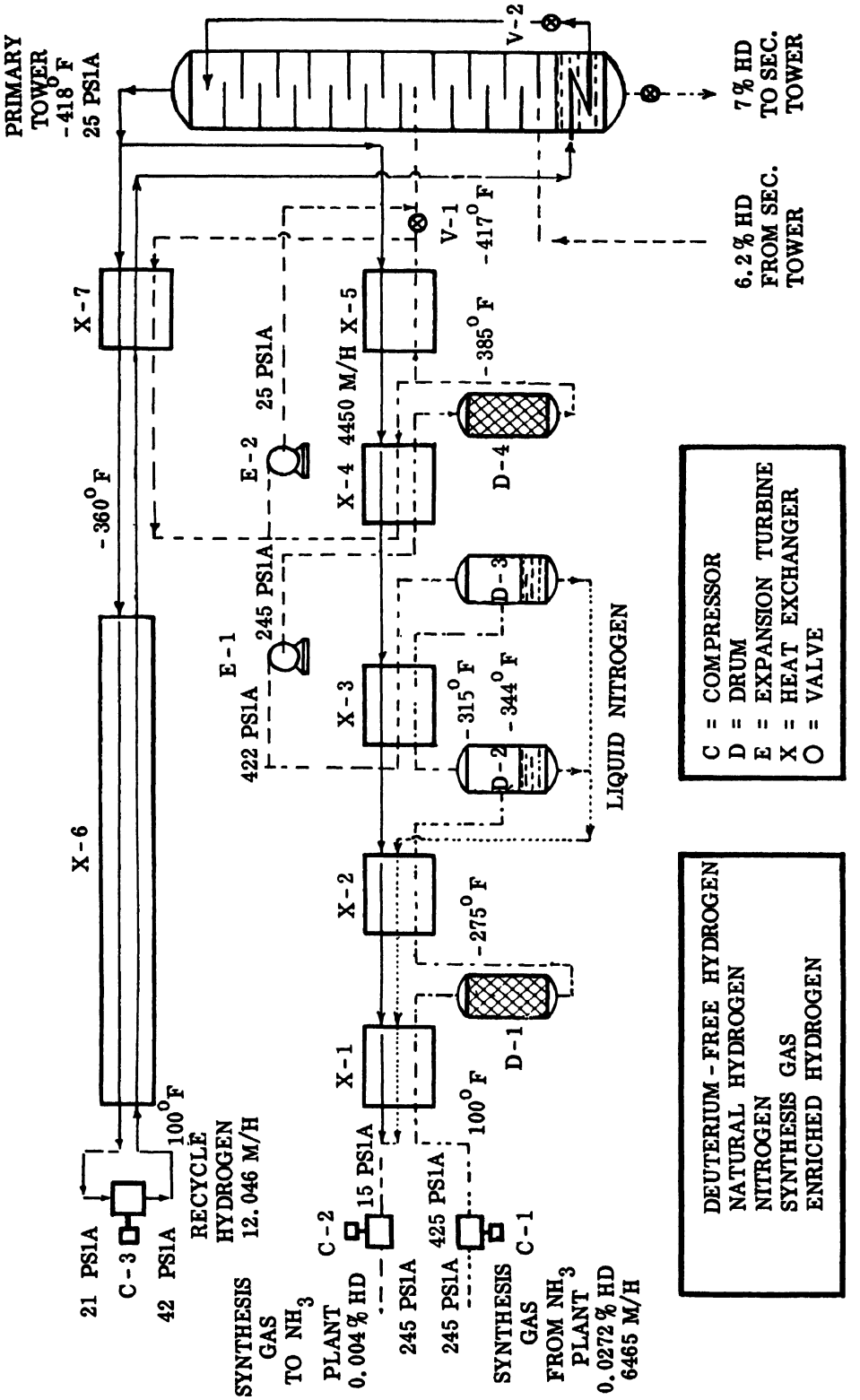

Figure 2. Flowsheet for primary section of HR: hydrogen distillation plant

tion, with 90% conversion of hydrogen to ammonia, and 86% recovery of deuterium from hydrogen, it would be possible to produce

$$\frac{20}{17} \times \frac{3}{2} \times \frac{0.86}{0.90} \times 0.000136 \times 2000 = 0.46 \text{ lb}$$

of heavy water per ton of ammonia.

The best location for a hydrogen distillation plant was thought to be the ammonia plant of the Phillips Chemical Co., at Etter, Texas. Factors favoring this plant were the low cost of natural gas fuel, 10¢/thousand cubic feet, and the relatively high rate of ammonia production, 440 tons per day at that time.

The Hydrocarbon Research hydrogen-distillation plant was designed for this location, but was sized to handle 20% more hydrogen than was then being produced. The product was to be heavy water containing no more than 0.25 atom % H. The design recovery was 86% of the 136 parts per million of deuterium present in the feed. The annual output of heavy water forecast was 34.2 tons, assuming 337 operating days per year.

Ammonia synthesis gas from the Phillips plant contained 72.2% H_2, 24.1% N_2, 2.7% CO, 0.2% CO_2, 0.4% CH_4, lesser quantities of argon, helium and neon, and variable amounts of oxygen and water. The gas was available at 245-psia pressure.

2.22 Process

Before entering the low-temperature plant proper, the CO_2 content of this gas would be reduced to 0.05% by scrubbing with caustic soda, and the oxygen content reduced to 1 ppm by passing the gas over palladium-on-alumina catalyst.

Figure 2 is a flowsheet illustrating the principal steps of the process for separating hydrogen from the remaining impurities (CH_4, N_2, CO, etc.), liquefying the hydrogen, and concentrating the deuterium to 7% HD. The rest of the HRI process, for fractional distillation of pure deuterium from this HD concentrate, is similar to that of Clusius and Starke described above, and will not be detailed. At the design feed rate this design would produce 0.535 moles of 99.75% D_2 per hour, corresponding to 256 pounds of D_2O per day.

Gas from the ammonia plant at a maximum rate of 6465 moles per hour is compressed from 245 to 425 psia. This gas is then cooled to liquid hydrogen temperatures by the succession of feed heat exchangers X-1 through X-5. Cooling is provided by the outgoing product gases, hydrogen stripped of deuterium and nitrogen. The first of these exchangers, X-1, cools the gas to the nitrogen dew point temperature, —275°F. While this gas is being cooled, all of the water and some of the carbon dioxide deposits in the feed passages of the heat exchanger. In order to prevent the exchanger from being fouled, the feed gas and the outgoing hydrogen gas are interchanged at 15-minute intervals so that the outgoing low-pressure hydrogen may re-evaporate the water and carbon dioxide deposited from the feed.

Feed then passes through the drum D-1 filled with silica gel to remove methane and the remaining carbon dioxide, to keep them from fouling equipment at lower temperatures.

In exchanger X-3 the gas is further cooled to to —315°F and most of the nitrogen is condensed as liquid. This nitrogen is separated in drum D-2. In exchanger X-3 the gas is further cooled to —344°F, which is close to the temperature at which nitrogen freezes, and a second smaller amount of liquid nitrogen is separated in drum D-3. The conditions of temperature (—344°F) and pressure (422 psia) selected for this separation of nitrogen from feed gas are those which leave the minimum possible concentration of nitrogen in the residual gas phase, according to the data of Verschoyle.[26] At this point the gas still contains 1.9% nitrogen, but has been freed of other condensible impurities.

The gas from D-3 is passed back through exchanger X-3 to provide additional cooling and then is expanded through the turbine E-1 to 245 psia to provide refrigeration at the —340° level.

The rest of the nitrogen in the gas must be taken out as solid. This is done by cooling the gas to —385°F in exchanger X-4. This exchanger, like X-1, is of the reversing type so that the solid nitrogen deposited from the feed gas may be re-evaporated at intervals by the outgoing low-pressure, deuterium-free hydrogen.

Traces of nitrogen in the gas leaving X-4 are removed in drum D-4, which is filled with silica gel.

Most of the hydrogen is then passed through the final feed exchanger X-5, where it is cooled to —417°F. A portion of this hydrogen is expanded through the turbine E-2 to 25 psia to provide refrigeration at the —417°F level. The rest of the hydrogen is expanded through the valve V-1 to cool tower feed to the hydrogen dew-point temperature of —419°F at 25 psia.

In the primary tower, hydrogen feed is fractionated into an overhead product containing 0.004% HD and a bottoms product containing 7% HD. The bottoms product is sent on to the secondary tower system for final concentration to 99.75% deuterium. The secondary tower system returns a stream containing 6.2% HD to the bottom of the primary tower.

Reboil heat for the primary tower is obtained by condensing hydrogen at 42 psia and —418°F in integral reboiler coils in the primary tower. Reflux for the primary tower is obtained by flashing the hydrogen condensed in the reboiler coils through valve V-2 into the top of the tower.

The overhead vapor from the top of the primary tower, containing 0.004% HD, is split. An amount corresponding to the incoming feed (4450 moles per hour) is returned through the feed exchangers X-5 through X-1. The rest of the hydrogen (12,046 moles per hour) is warmed to room temperature

through exchangers X-7 and X-6, compressed to 42 psia, and recycled back through this exchanger system to provide reboil heat for the bottom of the primary tower.

Nitrogen and hydrogen leaving the warm end of exchanger X-1 at substantially atmospheric pressure are recompressed to 245 psia and returned to the ammonia plant.

The over-all effect of the process then is that synthesis gas from the ammonia plant is separated into nitrogen and hydrogen, the hydrogen is liquefied, the deuterium is extracted, and nitrogen and deuterium-free hydrogen are returned to the ammonia plant. In the HRI design it was estimated that 98.5% of the synthesis gas could be returned to the ammonia plant.

2.23 Plant Design

All of the equipment operating below ambient temperature is housed in a cold-box containing Santocel or Pearlite insulation at least five feet thick. The cold-box is filled with hydrogen at a few inches of water gauge pressure.

The primary tower, the largest single piece of equipment in the plant, is an 80-tray bubble-cap tower, 13 feet in diameter by 141 feet high. An integral reboiler is built into its sump. The portion of the tower projecting through the roof of the cold-box is insulated by an 18-inch annular vacuum jacket filled with Santocel.

The secondary towers of the plant are packed with stainless-steel Stedman packing. Fookson *et al.*[8] have shown that this packing is very effective for separating H_2, HD and D_2, with a height equivalent to a theoretical plate of 1.0 inches.

The principal heat exchangers used in this plant are listed in Table II.

Three types of heat exchangers used in this plant are: the shell-and-tube type, the flat-plate type and the harp type. The reboiler is of the shell-and-tube type with copper tubes in a stainless tube sheet. The flat-plate type is conventional in low-temperature plants and consists of alternate layers of corrugated extended surface and the flat sheets which separate adjacent gas passages. It is the most economical form of extended surface for low-temperature plants, but is limited to pressure of the order of 100 psia. For higher pressures the harp type is used. This consists of concentric vertical tubes brazed to radial fins. The tubes are connected in banks by horizontal headers.

The operability of this process depends on the efficiency of the expansion turbines which provide low-temperature refrigeration for the plant. These were specified to be of the three-stage, radial-reaction type, in which work done by the hydrogen gas is transferred by a shaft to an oil pump operating outside of the cold part of the plant. An over-all expander efficiency of 74% was guaranteed by the prospective manufacturers.

All low-temperature piping in the plant was to be made of extra-low-carbon stainless steel. Special brazed connections were developed for leak-tight connections to aluminum heat exchangers.

2.24 Utilities

The estimated refrigeration balance for this plant is given in Table III.

The total power demand of this plant to drive the gas compressors was estimated to be 18,100 kw. This corresponds to 1690 kwh/lb, or 3.7 kwh/gm of heavy water, somewhat less than the estimate of Clusius and Starke.

2.25 Problems

The most serious problems encountered during the design of this plant were: (1) the removal of nitrogen from feed hydrogen; (2) suppression of the conversion of ortho to para hydrogen; and (3) lower relative volatilities for H_2-HD mixtures than originally anticipated.

Removal of Nitrogen

Nitrogen has a triple-point pressure of 1.86 psia at −346°F. Gases containing nitrogen can be cooled to about −344°F without risk of plugging heat exchangers with frozen nitrogen. In hydrogen saturated with nitrogen at this temperature, Verschoyle's[26] measurements indicate that the lowest attainable nitrogen concentration is about 1.9 mole %, at pressures between 300 and 500 psia. This is the nitrogen concentration in gas entering reversing exchanger X-4. More than one ton per hour of solid nitrogen must be condensed in this exchanger. The exchanger must be designed with sufficient free volume to accommodate solid nitrogen without plugging, in such

Table II. Principal Heat Exchangers of Hydrogen Distillation Plant

Number (Figure 2)	*Type*	*Duty, million BTU/hr*	*Surface ft²*	*Materials*
X-1	Reversing, harp	16.3	332,000	Al
X-2	Harp	4.5	52,000	Al
X-3	Harp	1.47	115,000	Al
X-4	Reversing, harp	1.06	131,000	Al and stainless
X-5	Harp	0.64	29,300	Al
X-6	Flat plate	34.1	1,412,000	Al
X-7	Harp	3.9	344,500	Al
Reboiler	Shell-and-tube	4.5	13,000	Stainless and copper

a way that the amount of high-pressure hydrogen held in the exchanger with the nitrogen is a minimum. Otherwise, the loss of feed gas vented from the exchanger when it is reversed would constitute an undue loss of feed and refrigeration to the process. Exchanger X-4 was designed with widely-spaced fins and a low heat transfer coefficient at the warm end, and with closer fins and a better coefficient at the cold end, so that it would fill nearly uniformly with solid nitrogen. In this way it was believed that the refrigeration loss on reversal could be held to 30,000 BTU, and the loss of feed could be held to 9%. The predicted deuterium recovery of 86% allows 5% loss in the overhead from the primary tower and 9% loss on exchanger reversal.

Ortho-Para Conversion

Normal hydrogen fed to this plant contains 75 mole % ortho hydrogen, or 3450 pound moles per hour. Since the heat released in the isothermal conversion of ortho to para hydrogen is 610 BTU per pound mole, complete conversion of the hydrogen in the feed would release 2.1 million BTU per hour, which exceeds the refrigeration capacity of the expanders. It is therefore vital to minimize the rate of conversion.

H. L. Johnston of Ohio State University measured the catalytic activity of metals to be used in the plant and of the silica gel proposed for use in the absorbers. The most serious conversion was found on silica gel, especially when carrying adsorbed oxygen. One pound of silica gel in normal hydrogen at 245 psia and −385°F will convert 0.004 pound moles of ortho hydrogen per hour. One pound of oxygen adsorbed on silica gel and exposed to hydrogen at the above conditions will convert 1640 pound moles of ortho hydrogen per hour. It is therefore important to use the smallest possible charge of silica gel and imperative to free the feed gas of oxygen so far as possible. The principal sources of conversion of ortho to para hydrogen expected in the proposed plant were:

Source	*Amount*	*Heat evolution, BTU/hr*
Stainless steel	48,000 ft²	4200
Silica gel (−275, −385°F)	10,050 lb	19,550
O_2 on silica gel (−275°F)	0.129 lb	60,000
Liquid hydrogen	5556 lb mole	17,500
Other		1250
Total		102,500

Relative Volatilities in Primary Tower

The key components in the primary tower are ortho hydrogen and HD. The ratio of their vapor pressures at the condition of this tower, 25 psia and −419.4°F, is 1.59. Unfortunately, the relative volatility of these components is predicted to be only 1.39 in solutions lean in HD. The reasons for the difference are: (1) hydrogen vapor at this temperature and pressure deviates from a perfect gas;[28] and (2) the activity coefficient of HD in liquid hydrogen is 1.075. This can be inferred[12] from measurements of the dew point of HD-H_2 mixtures[11] which showed positive deviations from Raoult's Law.

The difference between relative volatilities of 1.59 and 1.39 means an increase of almost 50% in the amount of reboil hydrogen required.

Table III. Refrigeration Balance

	BTU/hr
Demand	
Enthalpy difference, warm end of heat exchangers	437,000
Purge loss during exchanger reversal	30,000
Cold material leakage	10,000
Heat leak	108,000
Cooling adsorbers	62,000
Partial conversion of ortho to para hydrogen	102,000
Total	749,000
Supply	
Turbine E-1	408,000
Turbine E-2	604,000
Total	1,012,000

2.26 Costs

The cost estimated for this plant was $9,300,000. To this must be added the cost of changes to the ammonia plant to bring the D content of hydrogen up to 136 ppm, which was estimated to be $775,000, and engineering charges and contractors' fees, which might have added $1,000,000. The total cost for this plant would have been in the neighborhood of $11 million, if built in 1951. If allowance is made for the subsequent increase in construction-cost index, the plant would cost $13.4 million if built today.

The annual cost of operating the plant was estimated to be slightly in excess of $1 million. This might be $1.3 million today. The annual output of the plant, if fed with synthesis gas available at Etter, Texas, was estimated to be 34.2 tons of heavy water. If the plant were built where more synthesis gas was available, it could produce up to 40 tons per year of heavy water. On this basis, the investment cost for a plant of this type, if built today, would be around $170 per pound of D_2O per year, and the operating cost would be $16 per pound.

2.3 Evaluation

Since these costs are lower than for the other heavy-water processes for which cost data are available, it is of interest to examine the present position of the hydrogen-distillation process. A plant built today would probably differ from the one described in two respects:

1. The cold box would be insulated by Santocel in vacuum rather than in a hydrogen atmosphere, to make possible complete purging of air originally present in the Santocel. This would probably mean smaller cold units, with lower unit capacity and higher unit cost.

2. A hydrogen-distillation plant could advantageously be made part of one of the new ammonia plants which purify synthesis gas by washing it with liquid nitrogen. This would provide feed for the

deuterium plant already freed of water, methane and CO_2 and precooled to −310°F. Substantial cost saving should thus be possible, which might offset the higher cost of a vacuum-insulated plant.

Such a plant, located at a large ammonia plant, should be an economical producer of heavy water in the ratio of 0.46 pounds of heavy water per ton of ammonia.

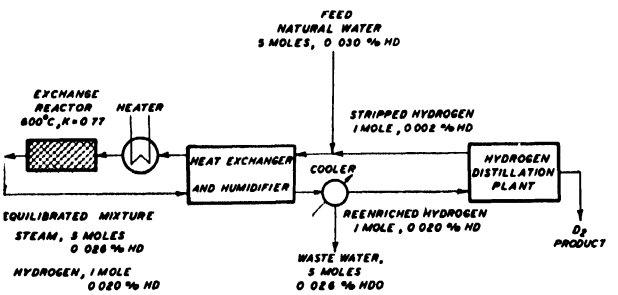

Figure 3. Distillation of hydrogen re-enriched by exchange with steam

A possible modification of the hydrogen-distillation process which would free the process from dependence on an ammonia plant for feed is described in the next section.

3. DISTILLATION OF HYDROGEN-FED DEUTERIUM BY EXCHANGE WITH STEAM

Figure 3 shows one means of freeing a hydrogen distillation plant from dependence on an ammonia plant for feed, though at an increase in cost and complexity. Hydrogen which has been stripped of deuterium in the distillation plant is mixed with an excess of steam, heated to an elevated temperature, and passed through a reactor where the exchange equilibrium

$$HDO + H_2 \rightleftharpoons HD + H_2O$$

is established by means of a catalyst. This increases the HD content of the hydrogen. The gases are then cooled to room temperature, the steam is condensed, the water separated, and the hydrogen, now somewhat re-enriched in deuterium, is recycled through the distillation plant.

Cerrai *et al.*[2] have proposed using this reaction to transfer deuterium from steam to hydrogen as part of a dual-temperature exchange process, to be described in Section 7. Equilibrium constants measured by these workers are: 100°C $K = 0.40$; 200°C $K = 0.50$; 300°C $K = 0.59$; 400°C $K = 0.66$; 500°C $K = 0.72$; and 600°C $K = 0.77$. They concluded that temperatures above 600°C would be impractical because catalysis by materials of construction then becomes rapid, so that the reaction would revert to equilibrium at 600°C as the gases were cooled down.

The mole fraction of HD in the feed to the distillation plant (x), is related to the moles of steam fed per mole of hydrogen recycled (S), the equilibrium constant (K), and the fraction of deuterium recovered in the distillation plant (r) by

$$x = \frac{0.0003\,KS}{(S + Kr)} \qquad (3.1)^*$$

The deuterium content of feed increases with increasing ratio of steam to hydrogen and with increasing K (higher temperatures).

The optimum temperature for the exchange reactor, the optimum ratio of fresh water to recycle hydrogen, and the optimum heat exchanger temperature difference are all points for engineering study which have not been settled. In the particular example shown in Fig. 3, a water/hydrogen molal ratio (S) of 5 and a catalyst temperature of 600°C, with $K = 0.77$, have been chosen. It is also assumed that 90% of the deuterium in the recycle hydrogen is recovered in the distillation plant.

Under these conditions, the mole % of HD in feed to the distillation plant ($100x$) is 0.02. This may be compared with 0.0272% when ammonia synthesis gas is used for feed.

This example shows that the distillation plant for a given deuterium output must be larger when recycle hydrogen is enriched by exchange with steam than when ammonia synthesis gas is used as feed. With recycle hydrogen, however, the distillation plant would be simple, because it would not be necessary to separate large amounts of nitrogen and other impurities from the hydrogen feed. A simpler exchanger system than shown in Fig. 2 would suffice, and reversing exchangers could be smaller, so that recoveries over 86% would be possible.

This combined exchange and hydrogen-distillation process is thought to have sufficient merit to warrant further attention.

4. DISTILLATION OF WATER

4.1 Separation Factor

Water contains the three molecular species H_2O, HDO and D_2O. In concentrating heavy water by distillation, the deuterium separation factor is defined as the ratio of the atomic ratios of deuterium to hy-

*Equation 3.1 is derived as follows: The equilibrium constant is

$$\frac{(HD)\,(H_2O)}{(H_2)\,(HDO)} = K \qquad (3.2)$$

where quantities in parentheses denote number of moles leaving exchange reactor. Also

$$(H_2O)/(H_2) = S \qquad (3.3)$$

because at the very low concentrations of deuterium this ratio is not significantly different from the ratio of steam to recycle hydrogen of both isotopic species. By definition

$$(HD)/(H_2) = x \qquad (3.4)$$

Since the (HD) + (HDO) remains constant in the exchange reaction

$$(HD) + (HDO) = (1 - r) \times (H_2) + 0.0003\,(H_2O) \qquad (3.5)$$

Equation (3.1) for x is obtained by eliminating (HD), (HDO), (H_2) and (H_2O) from (3.2), (3.3), (3.4) and (3.5).

drogen in the liquid to the corresponding ratio in the vapor. In terms of the mole fractions of individual compounds in the liquid (x) and vapor (y), the separation factor (α^*) is

$$\alpha^* = \left[\frac{x_{HDO} + 2x_{D_2O}}{2x_{H_2O} + x_{HDO}}\right]\left[\frac{2y_{H_2O} + y_{HDO}}{y_{HDO} + 2y_{H_2O}}\right] \quad (4.1)$$

Urey [24] has shown that α^* may be expressed in terms of the vapor pressures (π) of H_2O and D_2O by

$$\alpha^* = \sqrt{\pi_{D_2O}/\pi_{H_2O}} \quad (4.2)$$

provided:

1. Liquid and vapor phases form ideal solutions.
2. The vapor pressure of HDO is the geometric mean of the vapor pressures of H_2O and D_2O.
3. The equilibrium constant for the reaction

$$H_2O + D_2O \rightleftharpoons 2HDO$$

in the vapor phase has the value 4.0.

4. This equilibrium is maintained in the liquid.

These assumptions are plausible, but are not subject to detailed experimental check because liquid HDO cannot be isolated, since it disproportionates into H_2O and D_2O. Combs, Googin and Smith[7] have measured the distribution of D and H between liquid and vapor phases and have shown that the observed separation factor is within a few parts per thousand of that predicted by (4.2). Their results are summarized in Table IV, together with a more extensive tabulation of vapor pressure ratios given by Kirshenbaum.[14] The latter results will be used in this work because of the greater temperature range covered.

Because α^* increases as pressure is reduced, there is a strong incentive to operate a water distillation plant at sub-atmospheric pressures. This is offset in part, however, by the larger towers required to handle a given mass flow rate of vapor at lower pressure. In practice, an economic balance must be made; in the Manhattan District water distillation plants, tower top pressures between 50 and 125 mm were used, corresponding to separation factors between 1.06 and 1.05.

Table IV. Deuterium Separation Factors in Distillation of Water

Temp. °C	Vapor pressure of H_2O mm Hg	Vapor pressure ratio, $\sqrt{\pi_{H_2O}/\pi_{D_2O}}$ Kirshenbaum[14]	Combs et al.[7]	Sep. factor[17]
0	4.58	1.12_0		
10	9.21	1.08_7	1.094	1.100_3
20	17.54	1.07_4	1.082	1.087_3
30	31.8	1.06_6	1.071	1.074_8
40	55.3	1.05_9	1.063	1.062_9
50	92.5	1.052	1.055	1.051
60	149.4	1.046		
70	233.7	1.040		
80	355	1.035		
90	526	1.030		
100	760	1.026		
120	1489	1.019		
140	2711	1.013_5		
160	4636	1.009		
180	7521	1.005		
200	11,661	1.002_5		
220	17,400	1.000_5		
240	25,100	0.997_9		

4.2 Process Requirements

A rough idea of the requirements of the water-distillation process may be derived from a representative separation factor of 1.05. The minimum number of theoretical plates (n_{min}) needed to enrich deuterium from the natural concentration of x_F=0.000149 atom fraction to product concentration of $x_P = 0.998$ is

$$n_{min} = \frac{\ln \dfrac{x_P(1-x_F)}{x_F(1-x_P)}}{\ln \alpha^*} = 308 \quad (4.3)$$

The optimum number will be somewhat more than twice this, or around 700 plates.

The minimum consumption of steam per mole of heavy water produced is secured when an infinite number of plates is used, so that the outgoing steam depleted in deuterium may be in equilibrium with incoming feed. Figure 4 illustrates the derivation of this minimum steam consumption. The deuterium material balance is

$$(S+1)x = Sy + x_P \quad (4.4)$$

or

$$S = (x_P - x)/(y - x) \quad (4.5)$$

When feed and depleted steam are in equilibrium

$$y = x/\alpha^* \quad (4.6)$$

so that

$$S = (x_P/x) - 1)\ \alpha^*/(\alpha^* - 1) \quad (4.7)$$

The minimum steam consumption per mole of heavy water is

$$\frac{S}{x_P} = \left(\frac{1}{x} - \frac{1}{x_P}\right)\frac{\alpha^*}{\alpha^* - 1} \cong \frac{\alpha^*}{x(\alpha^* - 1)} \quad (4.8)$$

The maximum recovery of deuterium in the feed (r)

$$r = \frac{x_P}{(S+1)x} = \frac{\alpha^* - 1}{\alpha^* - \dfrac{x}{x_P}} \cong \frac{\alpha^* - 1}{\alpha^*} \quad (4.9)$$

With $\alpha^* = 1.05$, $x = 0.000149$, and $x_P = 1$, we have for distillation of water: minimum moles steam per mole D_2O = 141,000; and maximum deuterium recovery ≐ 0.0475.

For a practical plant with the optimum number of stages, around 200,000 moles of steam must be provided per mole of heavy water produced.

From these rough figures, it is apparent that a water-distillation plant will need a large number of

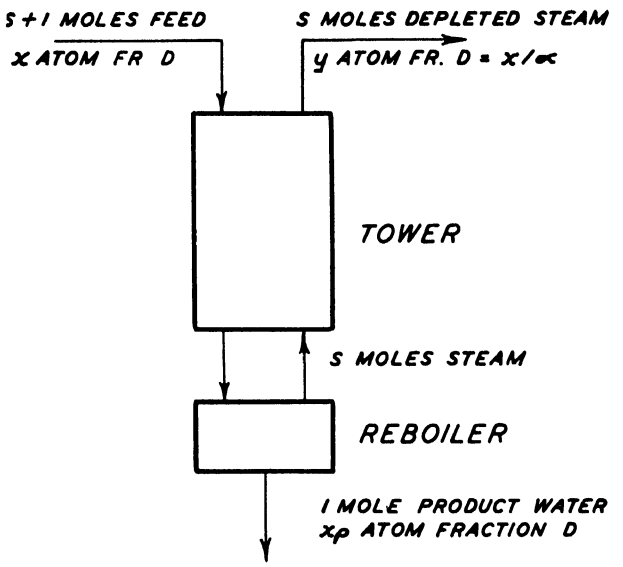

Figure 4. Minimum steam consumption in distillation

towers and will consume a large amount of steam in comparison with its output.

4.3 History of Process

Despite these severe requirements, the water-distillation process is of interest because of the simple equipment used. It has received attention in Germany, where pilot-plant work was done by I. G. Farben during the last war,[6] in New Zealand, where a water-distillation plant is now being built as part of an electric power plant using low-cost geothermal steam as a heat source, and in the United States, where most of the heavy water used by the Manhattan District was produced in this way.

4.4 Manhattan District Plants

The water-distillation plants of the Manhattan District were built to provide a simple and certain way of producing heavy water, though not necessarily at minimum cost. Because speed was more important than economy, it was not possible to explore fully developments which might have permitted more economical production. These plants are described briefly in this section, and modifications in future water-distillation plants which might be made to reduce costs are taken up in Section 4.5. More detailed information regarding the Manhattan District plants has been given by Maloney and Ray,[16] and by Selak and Finke.[19]

4.41 Plants

Three water-distillation plants were designed and built for the Manhattan District by the E. I. duPont de Nemours & Co., Inc. These plants were located at Morgantown Ordnance Works, Morgantown, W. Va.; Alabama Ordnance Works, Childersburg, Ala.; and Wabash River Ordnance Works, Newport, Ind. Parts of the plants were started up in June 1943, and concentrations reached steady-state values in June 1944. About 90 days were needed to reach steady state. The plants were shut down in October 1945 because of reduced demand and because of the high cost of their heavy water compared with the plant at Trail, B.C., to be described in Section 6.

These distillation plants concentrated deuterium from 0.0143 atom % to 87–91 atom %. Further concentration to 99.8% was effected by electrolysis. The average recovery of D_2O from the steam fed was only 1.94%. 360,000 moles of steam were fed per mole of D_2O produced.

The combined production capacity of the three plants was 1.20 tons per month. The total production of 99.8% D_2O was 22.8 tons.

The total cost of the plants was $14.5 million. The unit investment cost was therefore $14,500,000/1.20 × 12 × 2000 = $504/lb/yr.

The operating costs were

	Per month	*Per pound D_2O*
	$	$
Steam	295,000	123
Other	127,000	53
Total	$422,000	$176

The purity, recovery, and production rate of heavy water achieved in these plants was less than design expectations; the design production rate for the three plants was 2.4 tons per month, and the design recovery was 4%. Tests made to determine the cause of the inferior performance showed that the plate efficiency of the distillation towers as originally installed was only 50%; the low efficiency was attributed to excessive leakage of water between the plates and tower wall and to an excessive hydraulic gradient

Table V. Towers of Morgantown Water Distillation Plant

Tower	*Number in parallel*	*Diam.*	*No. of plates*	*Lb vapor per hour*	*Pressure, mm Hg* Top	Bottom	*Atom % D, bottom*
1A	5	15 ft.	80	(177,000)	67	238	
1B	5	12 ft.	90	177,000	236	536	0.117
2A	1	10.5 ft.	72	(21,200)	129	340	
2B	1	8 ft.	83	21,200	340	645	1.40
3	1	3.3 ft.	72	3050	124	343	3.8
4	1	1.5 ft.	72*	725	127	440	10.0
5	1	10 in.	72*	190	127	340	11.5
6	1	10 in.	72*	185	124	328	21.2
7	1	10 in.	72*	200	124	333	56.4
8	1	10 in.	72*	200	127	308	89
Total	18		757	202,750			

* Number of theoretical plates in packed column.

which caused part of each plate to have insufficient depth of liquid. When changes to correct these deficiencies were made in some of the towers, efficiencies were improved to 75%. If these changes had been made in all of the large towers, it was predicted that the deuterium recovery and plant capacity could have been doubled, at an estimated cost for revisions of $2,200,000. The plants were shut down before the revisions could be made.

4.42 Process

A simplified flowsheet of the process used at the Morgantown plant, the smallest and most efficient of the three, is shown in Fig. 5. This plant produced 560 pounds of D_2O per month, with a deuterium recovery of 2.8%. The plant consists of an eight-stage cascade of distillation towers, with associated reboilers, condensers and pumps. Summary data on the towers of each stage is given in Table V.

The first stage consists of 5 parallel groups of two series-connected towers, of which one group, 1A and 1B, are shown in the figure. Feed for each 1A tower consists of condensate from the reboiler of the associated 1B tower. Feed is introduced at the top of the 1A tower. Stripped vapor from the top plate is condensed in a barometric condenser, vented to a steam ejector which maintains a pressure of from 50 to 90 mm at the top of the tower.

Slightly enriched water from the bottom of tower 1A is pumped to the top of tower 1B, and vapor from the top of 1B flows back to the bottom of 1A.

Most of the water at the bottom of 1B, now enriched to 0.117 atom % D, is converted to vapor in the reboiler and returned to 1B, but around 12% is pumped ahead to the top of 2A. Vapor from the top of 2A is condensed in a condenser refrigerated with ammonia, to prevent loss of the now valuable water. This condenser is also vented to a steam ejector, which maintains a pressure of 130 mm.

The second stage consists of two towers, 2A and 2B, connected in series, like each 1A and 1B pair. The third and higher stages consist of single towers, of progressively decreasing diameter. Arrangements for reboiling water at the bottom of each tower and condensing and returning vapor at the top of the next stage are the same as at the bottom of 2B and the top of 3.

As the water flows through the stages of the plant, it is enriched progressively in deuterium, until it reaches 89 atom % in the bottom product of the eighth and last stage.

Most of the steam for the plants at Morgantown and elsewhere was generated at 150 psig and throttled to 40 psig, the pressure at which it was used in the reboilers, even though steam at 6 to 7 psig would have sufficed to reboil the tower bottoms, which were at subatmospheric pressure. Since low-pressure, by-product steam was not available in the required amounts, it was necessary to generate steam solely for the water-distillation plant. This could be done more economically at 150 psig than at lower pressures.

4.43 Towers

Towers of these plants over 18 in. in diameter were of the plate type, with plates on one-foot spaces. All of the large towers used bubble caps, except 1A, which had tunnel caps. Towers 18 in. in diameter and smaller were packed with $\frac{5}{8} \times \frac{5}{8}$ in. ceramic rings.

4.5 Possible Improvements in Water-Distillation Process

Two major improvements which could be made in any future water-distillation plant are:

(1) The use of tower internals with greater capacity per unit volume than tunnel- or bubble-cap plates, to increase plant capacity for the same capital investment.

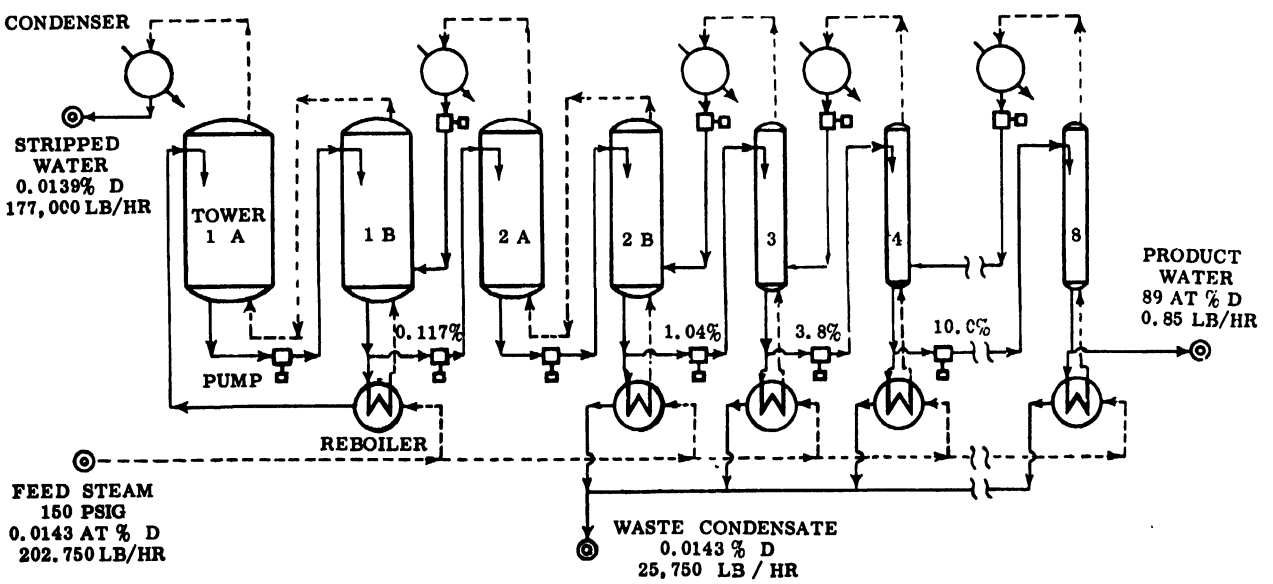

Figure 5. Morgantown water distillation plant

(2) More efficient utilization of heat than generating 150-psig steam solely for the distillation plant.

4.51 Packed Towers

Since these plants were built, several improved types of tower internals have been developed. A metal lath packing developed by Scofield[18] costs no more per cubic foot than bubble caps, and provides several times the capacity of bubble caps per unit volume. A similar packing known as "Spraypak," with specially shaped orifices, has been developed by the British Atomic Energy Research Establishment,[3,9,17] especially for the water-distillation process. Spraypak is to be used in the New Zealand distillation plant.

Table VI compares the predicted performance of Spraypak with the observed performance of one of the revised bubble-plate towers of the 2B group at Morgantown, for conditions at the top of this tower. Although the height of an equivalent plate (h) for Spraypak is somewhat higher than for the bubble-plate tower, the allowable velocity (u) for Spraypak is much higher.

The ratio u/h measures the steam flow rate through unit volume of a tower one-theoretical-plate high. This ratio for Spraypak is 3.6 times as great as for the Morgantown improved-bubble-plate towers. Thus a distillation plant with towers of the same volume as the Manhattan District plants, packed with Spraypak, should produce 3.6 times as much heavy water as the Manhattan District plants using improved bubble plates, or 7.2 times as much as the original plants, assuming that the improved bubble plates would double the deuterium recovery. Since the cost of these plants is largely in the towers, and the cost per unit volume of Spraypak ($20 per ft^3) is about the same as bubble-plates, these two distillation plants should cost about the same.

The pressure drop per theoretical plate for Spraypak is slightly less than for the bubble plates.

4.52 More Efficient Utilization of Heat

In the first-stage towers of the Manhattan District plants, where most of the heat was consumed, heat flowed from the tower bottom temperature of 195°F (10.5 psia) to the tower top temperature of 111°F (1.3 psia). To transfer this heat through the reboilers, steam at 233°F (22 psia) was required. Since this heat is needed only at relatively low temperatures, it is very inefficient to obtain it by burning fuel under boilers, without making use of the heat at higher temperatures first. Two possible ways of providing low-temperature heat more efficiently are: (1) using 22-psia exhaust steam from the turbines of a power plant; and (2) using a vapor-recompression system.

Examples of these two schemes are shown in Figs. 6 and 7. The turbine-exhaust scheme of Fig. 6 has two advantages over the vapor-recompression scheme of Fig. 7: (1) the cost of the condenser and steam jet ejector is less than that of the vapor compressor and feed-water preheater; and (2) the power lost in the steam turbine plant is less than the power

Table VI. Comparison of Bubble-Plate Towers with Towers Packed with Spraypak at 277.5-mm Hg, 165°F, and 0.0145 lb/ft^3 Vapor Density

	Bubble cap plates (12 ft dia)	*No. 5 Spraypak*
Steam rate, lb/hr	35,000	—
Steam velocity, ft/sec (u)	6.7	31.35
Plate spacing, ft	1.0	—
Plate efficiency	0.71	—
Height equiv. theor. plate (h)	1.4 (= 1.0/0.71)	1.8
Cubic feet of steam per second through unit volume of tower one theor. plate high (u/h), sec^{-1}	4.8	17.4
Pressure drop per ft, mm Hg (P/dz)	3.5	—
Pressure drop per theor. plate (hdP/dz)	4.9	4.7

consumed by the vapor compressor. Although the theoretical work, W, lost by the turbine exhausting at 22 psia instead of at 1.3 psia is exactly the same as the work consumed by a compressor taking the same amount of steam from 1.3 to 22 psia, the actual turbine efficiency of E drops the turbine work lost to WE, and the compressor efficiency of E' raises the work consumed by the compressor to W/E'.

The turbine-exhaust scheme has the disadvantage of making the production rate of heavy water dependent on the production rate of power from the steam turbines. The following example will illustrate the approximate relation between the two production rates. The assumptions are:

1. Deuterium recovery (r) = 3.88%, the value predicted for the Manhattan District plants with revised tower internals.
2. D content of feed water (x) = 0.000143 atom %.
3. Steam turbine plant thermal efficiency (e) with exhaust at 1.3 psia (571°R) is 35%.
4. ($1 - e$) is proportional to absolute exhaust temperature, so that at 22 psia (693°R)

$$1 - e = (1 - 0.35)693/571 = 0.789 \quad (4.10)$$

5. Latent heat of vaporization at 10.5 psia = 981 BTU/lb.
6. The ratio of total steam consumed to stripped

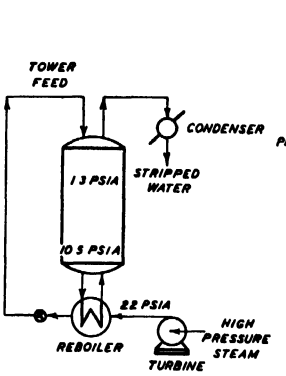

Figure 6. Water distillation tower reboiled by steam turbine exhaust

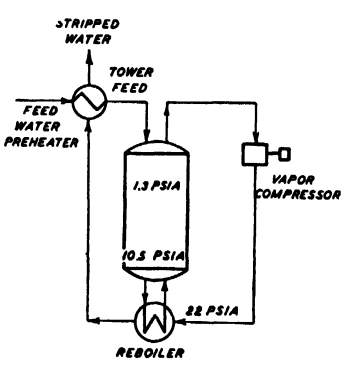

Figure 7. Water distillation tower reboiled by vapor recompression

steam from stage 1 is the same as at Morgantown, 202,750/177,000 = 1.145.

The number of pounds of steam required to produce one pound of heavy water is

$$\frac{18}{20} \times \frac{1.145\,(1 - xr)}{xr} = \frac{18}{20} \times \frac{1.145}{0.000149 \times 0.0388} = 178{,}000 \quad (4.11)$$

The amount of work in kwh which could be done by this amount of heat in the assumed power plant exhausting at 22 psia is [178,000 × 981 × (1 — 0.789)]/3413 BTU/kwh = 10,800 kwh.

Thus, production of one pound of heavy water by distillation requires the associated production of around 10,000 kwh of power in this arrangement. If heavy water sells for $50 per pound and power for 5 mils per kwh, the value of both products will be the same.

4.53 Costs

A rough indication of what heavy water should cost in a water-distillation plant using these two improvements may be made with the aid of the following assumptions.

1. Tower volume is same as combined Manhattan District plants.
2. Heavy-water production rate is 7.2 times that of MD plants, as derived in Section 4.51.
3. Total plant cost is same as combined MD plants adjusted for change in construction-cost index (141.37 in September, 1943 to 314.17 in May, 1955).
4. Monthly operating costs, except steam, are same as in MD plants.
5. High-pressure steam for power plant costs $0.40 per thousand pounds.

The unit investment cost under these assumptions would be

$$\frac{504}{7.2} \times \frac{314.17}{141.37} = \$155/\text{lb/yr}$$

The charge to the heavy-water plant for 22-psia steam may be found as follows:

If the power plant exhausting steam at 22 psia uses 1000 pounds of steam, it would have used 21.9/35 × 1000 = 625 pounds of steam when exhausting at 1.3 psia. The cost of the additional 375 pounds of steam is 375 × $0.40 = $0.15. This is the charge to the heavy-water plant for 1000 pounds of 22-psia steam.

The unit operating cost is then derived as follows: steam: 178,000 lb at $0.15 per 1000 lb = $26.7/lb D_2O; other costs: $53/lb (MD) ÷ 7.2 = 7.4, and total: $34.

5. ELECTROLYSIS OF WATER

5.1 History of Process

When water is decomposed electrolytically into hydrogen and oxygen, the deuterium content of the hydrogen produced at the cathode is substantially lower than that of the water remaining in the cell. As electrolysis continues, the water becomes progressively enriched in deuterium, in very much the same way as evaporation of a mixture of benzene and toluene leaves a residue enriched in the less volatile toluene. The gas produced in the latter stages of electrolysis is richer in deuterium than the water initially fed; if desired, this gas may be burned and the water condensed and returned to the cell.

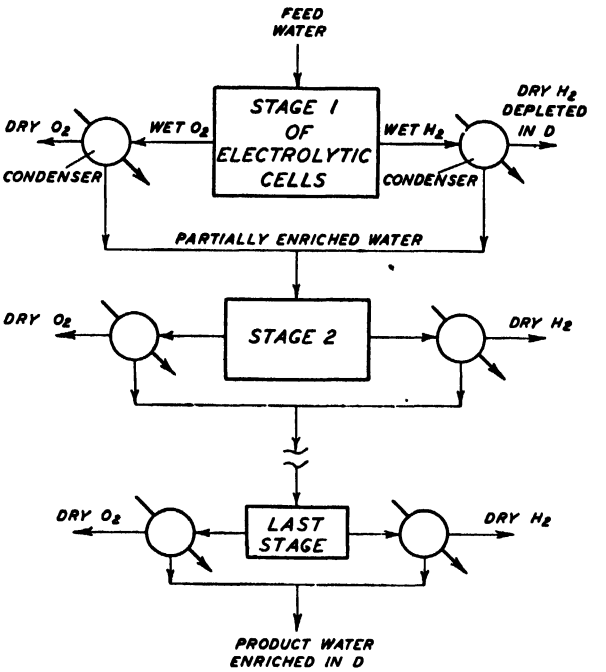

Figure 8. Steady-flow cascade of electrolytic cells, without recycle

Until 1943, all of the heavy water produced commercially was made by electrolysis. The largest single producer of heavy water was the Norsk Hydro Co., which operated the world's largest electrolytic hydrogen plant at Rjukan, Norway. In 1942, this plant was making about 1.7 short tons of heavy water per year as a byproduct of the production of 640,000 std ft^3 of electrolytic hydrogen per hour, used for ammonia synthesis. The average power consumption of this plant was 91,000 kw, or 54 kwh per pound mole of hydrogen.

The primary plant at Rjukan made water containing 15 atom % D. The electrolytic cells were of the Pechkranz type, with steel cathodes and diaphragms to prevent mixing of hydrogen and oxygen. Nine stages of parallel-connected cells were used, with the number of cells per stage decreasing as the deuterium content increased. The stages were connected in a series cascade, without recycle of partially enriched hydrogen, and the cascade was operated in steady flow. A schematic flowsheet for this kind of plant is shown in Fig. 8. About 73% of the water fed to each stage was electrolyzed; and 27% was carried from the stage by the products of electrolysis as water vapor, condensed, and fed to the next higher stage of the cascade. The fraction of water fed for-

ward is controlled by the vapor pressure of water; 27% forward feed requires an electrolyte temperature of 60°C.

The product of the primary plant was refined to pure D_2O in a small, nine-stage secondary plant, also operated with steady flow, but with the partially enriched hydrogen burned and recycled, as shown in Fig. 9.

The electrolytic process was also used by the Manhattan District, at Morgantown, W. Va., and at Trail, B. C., but only to refine crude heavy water from a primary plant where some process other than electrolysis was employed. These electrolytic plants were operated batchwise. The cells had no diaphragms, so that the product was a mixture of hydrogen and oxygen. The gases were recombined in a burner and the water was recycled to the primary plant when its deuterium content was leaner than primary-plant product and to the next batch of the electrolytic plant when its deuterium content was richer than primary-plant product.

At Morgantown, 1.2 tons of 99.7% D_2O per month was produced from the product of the water-distillation plant which contained 87–91 atom % D. After purification, this water was mixed with K_2CO_3 electrolyte to form a 7.5 wt % solution, which was kept at 40°C during electrolysis. Electrolysis of about 55% of the water raised its D content to 99.7%. The water was then evaporated from the K_2CO_3. The hydrogen and oxygen gases were recombined, and the resulting water was divided into lots according to isotopic content. These lots were added to the next batch electrolyzed when the electrolyte and water had the same deuterium content.

The secondary plant at Trail is still in operation. In 1945, 0.5 ton of 99.8% D_2O per month was produced from the product of the primary exchange plant, which contained 2.14 atom % D. Because of the wide composition range, three batch stages were used, with 126, 20 and 4 electrolytic cells per stage. The electrolyte charge at the beginning of a batch was 2.5 wt % KOH. The electrolyte is kept at 23°C during electrolysis. In the first two stages 85% of the water per batch is electrolyzed; in the third stage, 67%. At the end of a batch the KOH is converted to K_2CO_3 by bubbling in CO_2, and the water is evaporated from it. Otherwise, operation is generally similar to the Morgantown plant.

Details of the Manhattan District's secondary electrolytic plants are given by Maloney and Ray.[16]

The primary-exchange plant at Trail, to be described in Section 6, uses hydrogen produced electrolytically by the Consolidated Mining and Smelting Co., for ammonia synthesis. This is the largest electrolytic-hydrogen plant in North America. In 1945, the average hydrogen production rate was 520,000 std ft^3 per hour, almost as great as at Rjukan. Cells were of the diaphragm type, with steel cathodes. The electrolyte was 28 wt % KOH or 20 wt % NaOH. Electrolyte temperatures of 60–70°C were used. The

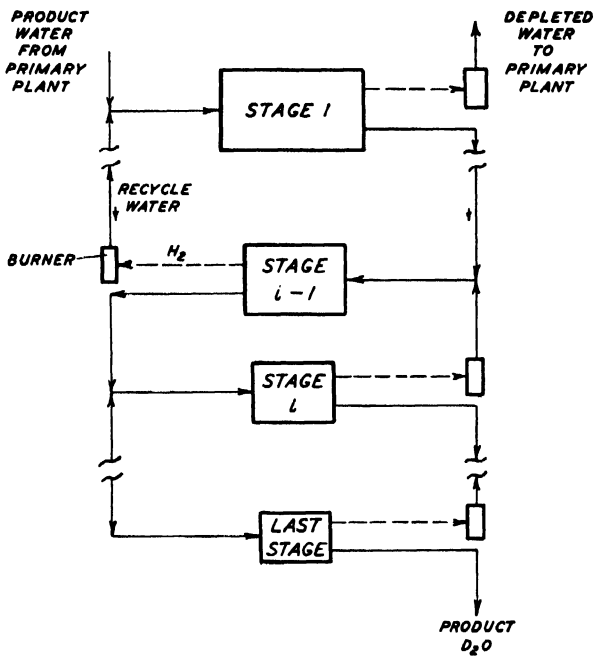

Figure 9. Steady-flow recycle cascade of electrolytic cells

cells were operated with steady flow. Since the principal means for isotope separation in the primary plant at Trail is by the exchange process rather than by electrolysis, no special efforts were made to obtain a high separation factor in the primary plant.

5.2 Separation Factor

Deuterium separation factors in the four electrolytic plants described above are listed in Table VII, together with operating conditions which may have an effect on separation factors. Separation factors of 6 to 8 realized in the two secondary plants are in the range of the best values reported in laboratory studies.[22] The lower values in the two primary plants may be due in part to the higher temperature, lower voltage, and presence of the diaphragm, all of which are known to reduce the separation factor in electrolysis. These are unavoidable conditions in a low-cost plant for the electrolysis of water. At Trail, however, it is known that inability to keep the electrode surfaces clean had an important additional effect in depressing the separation factor, and it is possible that this was significant at Rjukan, also. In the secondary plants, the electrodes could be readily cleaned between batches.

Since the equilibrium constant for the reaction

$$H_2O\ (l) + HD\ (g) \rightleftharpoons HDO\ (l) + H_2\ (g)$$

is 3.88 at 25°C and 2.73 at 100°C, it is apparent that the separation factors up to 8 observed in electrolysis must be due to some mechanism other than establishment of equilibrium in this reaction at the cathode surface. One plausible explanation is that the hydrogen ion is discharged more readily at the cathode than the deuterium ion, thus accounting for the tendency of hydrogen to concentrate in the gas. This explanation is given support by laboratory find-

ings[22] that the separation factors up to 7.5 may be had under conditions of irreversible electrolysis, with high current densities or with electrode materials that do not catalyze this reaction. At low current densities, or with electrodes that catalyze the above

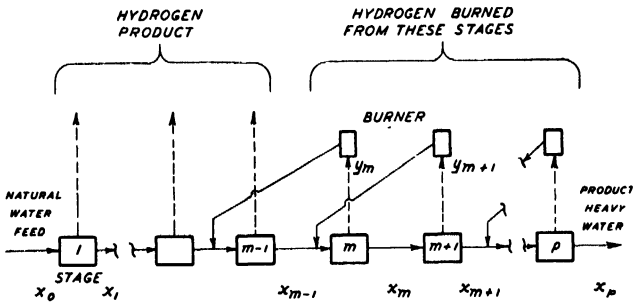

Figure 10. Electrolytic plant with hydrogen burned and recycled on upper stages

reaction, separation factors in electrolysis around 3, the equilibrium constant for this reaction, are observed.

5.3 Evaluation of Electrolytic Process

Because of its high separation factor and the ease with which it can be operated on the small scale, the electrolyte process is without equal for the refining of partially concentrated heavy water. Its usefulness for production of heavy water from natural water, however, is severely limited by the large amounts of water to be handled in such a case and the high unit costs of electrolysis. To show the limitations of electrolysis, it is of interest to estimate the maximum amount of heavy water which can be produced economically as byproduct of an electrolytic hydrogen plant.

The somewhat optimistic assumption will be made that a separation factor of 7 can be obtained without increasing the cell voltage above 2.1, perhaps by proper surface treatment of the electrodes. This voltage corresponds to 54 kwh per pound mole of water electrolyzed, at 95% current efficiency, or 142 kwh per thousand standard cubic feet of hydrogen produced.

As a specific example, we may consider a plant designed to produce 10,000 pound moles of hydrogen per day, while recovering as a byproduct as much heavy water as can be economically justified. The atom fraction D in feed water, x_0, will be taken as the natural value of 0.000149, and the atom fraction D in the heavy water product, x_P, will be taken as 0.99687 (to make the number of stages come out even). The flowsheet of series-connected electrolytic cells shown in Fig. 10 will be assumed, with hydrogen from the lower stages being used as the principal plant product and with hydrogen from the upper stages being burned and recycled to increase recovery of heavy-water byproduct. The principal variables in such a flowsheet are: (1) the increase in deuterium content taken per stage; and (2) the deuterium content, v_m, at and above which hydrogen is burned and recycled.

The increase in deuterium per stage is measured by the stage enrichment factor, β, defined in terms of the atom fraction D in the water leaving this stage, x_m, and the atom fraction D in the water leaving the next lower stage, x_{m-1}, as

$$\beta = \frac{x_m(1 - x_{m-1})}{x_{m-1}(1 - x_m)} \tag{5.1}$$

The optimum enrichment per stage for this flowsheet is that which causes the water from the next lower stage and recycle water from the next higher stage to have the same deuterium content:

$$x_{m-1} = y_{m+1} \tag{5.2}$$

so that there will be no loss of separation through mixing streams of different isotopic content. Since y_{m+1} and x_{m+1} are related by the stage separation factor α:

$$\alpha = \frac{y_{m+1}}{y_{m+1}} \frac{(1 - x_{m+1})}{(1 - x_{m+1})} \tag{5.3}$$

it is evident that for (5.2) to hold we must have

$$\beta^2 = \alpha \tag{5.4}$$

if β is to have the same value on every stage.

We will use condition (5.4) to set the enrichment per stage in the lower stages in which hydrogen is not recycled, also. The total number of stages, n, is then given by

$$n = 2\frac{\log \dfrac{x_P}{x_0}\dfrac{(1 - x_P)}{(1 - x_0)}}{\log \alpha} \tag{5.5}$$

Table VII. Separation Factors in Electrolytic Heavy-Water Plants

	Rjukan	*Trail*		*Morgantown*
	Primary	*Primary*	*Secondary*	*Secondary*
Cell diaphragm	Yes	Yes	No	No
Cathode	Steel	Steel	Steel	Steel
Electrolyte: material	KOH	KOH NaOH	KOH	K_2CO_3
initial wt %	—	28 20	2.5	7.5
final wt %	—	28 20	15	15
Temperature	~ 60	60–70	23	40
Voltage	2.1	2.1	2.6	2.6–3.4
Separation factor	5.3	3	8	6.0–8.2

which for the specific separation under consideration is

$$n = 2\frac{\log\left[\frac{0.99687}{0.000149}\,\frac{0.999851}{0.00313}\right]}{\log 7} = 15 \quad (5.6)$$

The deuterium content of hydrogen and water leaving the lower stages of this cascade is given in Table VIII.

It evidently would not pay to burn and recycle hydrogen from stages 1 and 2, because it is no richer in deuterium than feed. To determine at which stage it would pay to begin to burn and recycle hydrogen, a number of alternative flowsheets have been worked out, with the most significant results summarized in the last three columns of Table VIII. In the first case listed, hydrogen is burned and recycled on stage 3 and all higher stages in the second on stage 4 and higher, etc. In each, the unburned hydrogen production rate has been held constant at 10,000 moles. For each case there has been evaluated: (1) the moles of hydrogen burned and recycled (H); and (2) the moles of heavy water produced (P).

To determine which of these cases is best economically, it is necessary to set a value on the hydrogen which is burned and therefore lost. A representative value for hydrogen produced commercially by reforming natural gas is \$0.50 per thousand cubic feet; an electrolytic plant would probably not be built unless it could sell hydrogen for this figure. Since 0.5 moles of oxygen are consumed per mole of hydrogen burned, it is necessary to set a value on this, too. A value of \$12 per ton, or \$0.50 per thousand cubic feet, will be used. The value of hydrogen and oxygen consumed is therefore \$0.75 per thousand cubic feet or \$0.285 per mole of hydrogen burned.

The next-to-the-last column of Table VIII gives $\Delta H/\Delta P$, the ratio of the additional hydrogen which must be made to the additional heavy water produced when hydrogen from an additional stage is burned and recycled. The last column gives the value of the additional hydrogen and the associated oxygen required to produce one pound of additional D_2O. This is obtained as $0.285/20 \times \Delta H/\Delta P$. Because of the high value of \$93 per pound of incremental D_2O made by burning hydrogen from stage 3, it is evident that it would not be economic to burn hydrogen from this stage. The incremental value of \$35 per pound for hydrogen from stage 4 is close to the cost of heavy water in competing processes. Burning hydrogen from stage 4 to increase heavy water production therefore might be justified. Burning hydrogen from stage 5 and higher would certainly be economic.

The average cost of hydrogen and oxygen burned to make heavy water in the most favorable case is

$$\frac{458 \times 0.285}{0.488 \times 20} = \$13.4/\text{lb } D_2O \quad (5.7)$$

Although other operations would add something to the cost, it is evident that electrolysis provides a way of making small amounts of heavy water at a very low cost as a byproduct of hydrogen and oxygen. The assumptions on which this is based should be restated: (1) the cost of producing hydrogen and oxygen by electrolysis is \$0.50 per thousand cubic feet; and (2) the separation factor can be increased to 7 without increasing the cost of electrolysis.

Figure 11 is a flowsheet for a plant for this most favorable case, in which hydrogen from stage 4 and higher is burned and recycled. The fraction of deuterium in the feed which is recovered is only

$$\frac{0.488}{10{,}000 \times 0.000149} = 0.327 \quad (5.8)$$

This low recovery is characteristic of the electrolytic process when used as the sole means of concentrating deuterium. As a result, the amount of heavy water which could be produced by electrolysis alone, even at a large electrolytic plant, is small.

The power consumption per unit of heavy water is enormous. At 54 kwh per mole of water electrolyzed, the plant of Fig. 11 would consume

$$\frac{54 \times 10{,}458}{0.488 \times 20} = 57{,}800\ \text{kwh/lb } D_2O \quad (5.9)$$

or 128 kwh/gm.

Table VIII. Electrolytic Plants for Production of 10,000 Moles of Hydrogen, with Heavy Water as Byproduct. Conditions: $\alpha = 7$, $\beta = \sqrt{7}$, 15 Stages.

Stage No. (i)	Atom % D in stage product: Hydrogen ($100\,y_i$)	Atom % D in stage product: Water ($100\,x_i$)	Moles hydrogen burned and recycled from this and higher stages (H)	Moles D_2O product (P)	($\Delta H/\Delta P$)	Value of hydrogen consumed to produce incremental D_2O, \$/lb D_2O
Feed	—	0.0149				
1	0.00563	0.0394	—	—		
2	0.0149	0.1042	—	—		
3	0.0394	0.275	1550	0.655	6530	93
4	1.042	0.725	458	0.488	2460	35
5	0.275	1.89	127.3	0.3535	940	13
6	0.725	4.84	35.7	0.256	361	5.1
7	1.89	11.88	10.3	0.1856	—	—
15	97.85	99.687	—	—	59	0.8
No recycle			0.0	0.0121		

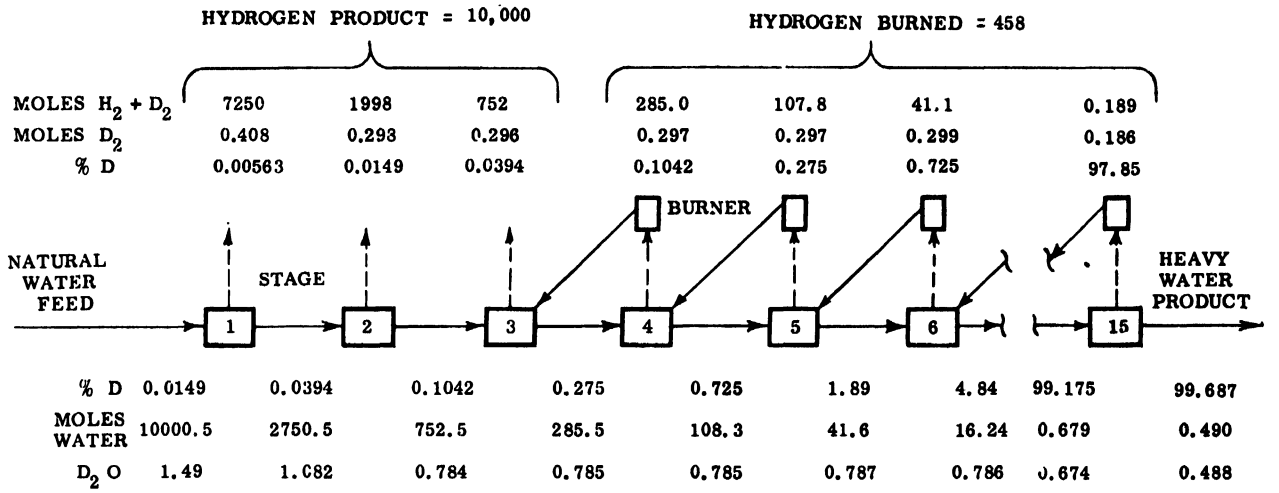

Figure 11. Optimum electrolytic cascade for production of 10,000 moles hydrogen and heavy water byproduct; $\alpha = 7$, $\beta = 7$

6. STEAM-HYDROGEN EXCHANGE

6.1 Principle of Process

In the electrolytic cascade shown in Fig. 11, 67.3% of the deuterium in the water fed leaves with the hydrogen product at too low a concentration for economic recovery by electrolysis, even though over half of the deuterium in the hydrogen product is at or above the natural abundance. Some of the deuterium in this hydrogen may be recovered economically by the steam-hydrogen exchange process. The principle of this process may be seen through an example. Consider the effect of mixing hydrogen from stage 3 of Fig. 11 containing 0.0394% D with an equal volume of steam containing the natural abundance of D, 0.0149%, and passing the mixture over a catalyst at 80°C in which the exchange equilibrium

$$HD + H_2O \rightleftharpoons H_2 + HDO$$

is established. Since the equilibrium constant for this reaction is 2.80 at this temperature, the deuterium content of hydrogen and steam will be changed as follows:

	% D	
	Before equilibration	*After equilibration*
Hydrogen	0.0394	0.0143
Steam	0.0149	0.0400

By cooling the mixture to condense the steam, and separating the hydrogen and water, it is possible to transfer deuterium from hydrogen gas to water *without* burning the hydrogen, and thus to increase the heavy-water output from an electrolytic plant without having to sacrifice hydrogen production. This principle would be applicable not only to hydrogen slightly enriched in deuterium, as from stage 3 of Fig. 11, but to any hydrogen containing more than 1/2.80 of the natural abundance of deuterium, since deuterium would be transferred to natural water from such hydrogen.

The variation of this equilibrium constant with temperature is given in Table IX. The theoretical values were used in the design of the Trail plant and the interpretation of its performance.

The exchange reaction proceeds at a negligible rate unless catalyzed, and the only catalysts thus far developed lose activity in the presence of liquid water. It is thus necessary to use a gas-phase catalytic reactor, as described in the previous example.

The recovery of deuterium from hydrogen by exchange with water can be increased over the single-stage example just cited by using a multistage countercurrent cascade. The simplest arrangement, consisting of a tower packed with catalyst through which liquid water flows down and gaseous hydrogen flows up is unfortunately not practical, because of the inactivation of catalyst mentioned above. One possible arrangement of gas-phase exchange reactors is shown in Fig. 12. In such a cascade each exchange reactor, with its associated evaporator, condenser, and separator acts like a single plate of a distillation column. If the condenser condenses all of the steam leaving a stage, the separation factor is simply the equilibrium

Table IX. Equilibrium Constant for Steam-Hydrogen Exchange Reaction
$H_2O + HD \rightleftharpoons HDO + H_2$

	Equilibrium Constant (K)	
Temp., °C	*Theoretical**	*Observed†*
0	4.19	–
25	3.62	–
50	3.20	3.05
75	2.88	2.77
100	2.63	2.55
125	2.43	2.36
200	–	1.98
300	–	1.69
400	–	1.52
500	–	1.39
600	–	1.30
750	–	1.21

* From Kirshenbaum.[13] Evaluated from molecular constants.

† Smoothed from experimental data of Cerrai *et al.*[2]

constant K for the above exchange reaction, with a value around 2.8. In such a cascade, the electrolytic cell acts like a reboiler to provide hydrogen recycle for the exchange cascade. In fact, the additional enrichment of deuterium occurring in the electrolytic cell is not essential for the operation of the process, since any desired degree of enrichment could be obtained by using a sufficient number of exchange stages in series.

The maximum recovery of deuterium from natural water possible with such a cascade as the number of stages is increased indefinitely is 64%, as may be determined from equation (4.9) with $\alpha = K = 2.8$. This is double the maximum recovery attainable economically by electrolysis alone. The deuterium content of hydrogen in equilibrium with natural water is 0.0053%.

6.2 History of Process

In 1941, the steam-hydrogen exchange process for enriching deuterium was proposed independently by Harteck and co-workers in Germany and by Urey and co-workers in the United States. Harteck and Suess[6,10] developed a supported nickel catalyst which caused the exchange reaction to take place at an acceptable rate below 100°C, where the equilibrium constant is favorable. In 1942, a set of exchange reactors containing this catalyst was installed to treat hydrogen from the sixth stage of the electrolytic plant at Rjukan, Norway,[21] and additional reactors were planned for the fourth and fifth stages, but operation was interrupted by the war before this could be completed.

In the United States the steam-hydrogen exchange process was the first selected for commercial development by the Manhattan District, and a heavy-water plant using this process was built at the synthetic ammonia plant of the Consolidated Mining and Smelting Co., at Trail, British Columbia. A nickel-chromia catalyst for the exchange reaction was developed by H. C. Urey and co-workers at Columbia University, and a platinum catalyst supported on activated carbon was developed by H. S. Taylor and co-workers at Princeton University. The exchange-tower system used in the Trail plant was devised by F. T. Barr and co-workers of the Standard Oil Development Co., who were responsible for the basic design of the plant. In September, 1942, construction of the exchange plant at Trail was started. The primary exchange plant and the secondary electrolytic plant (see Section 5) started operation in June, 1943. Deuterium concentrations reached steady values in September, 1944; the delay is due to the long equilibrium time of this process, around 8 months. By 1945, the plant was producing 1100 lb of 99.8% heavy water per month. It is still in operation.

6.3 The Trail Plant

6.31 Towers

The cascade of Fig. 12 has the disadvantage of requiring the production and condensation of a volume of steam equal to the volume of hydrogen being

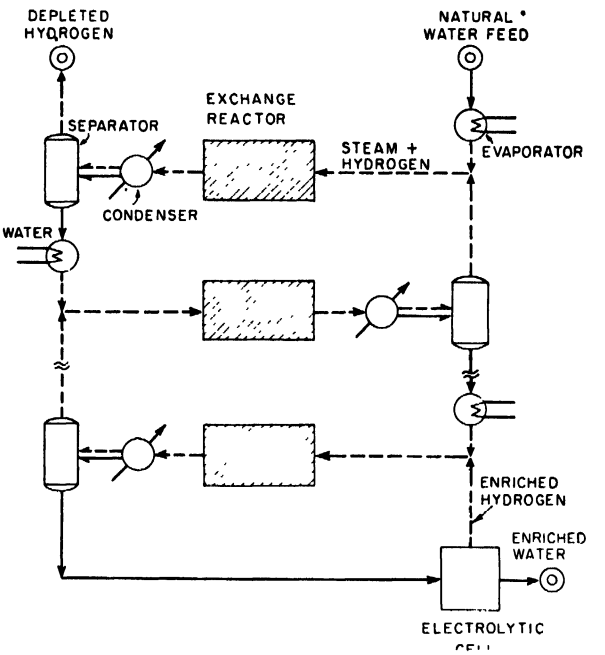

Figure 12. Cascade of exchange reactors

treated *times* the number of stages in the plant. To reduce this steam requirement, the Trail plant uses the tower arrangement shown in Fig. 13. A gaseous mixture of steam and hydrogen flows up this column, passing alternately through a pair of bubble-plate absorption trays, a heater to vaporize entrained water, a chamber filled with catalyst, another pair of absorption trays, another catalyst chamber, and so on through the top pair of absorption trays. Water flows down the column through the top pair of absorption trays, then bypasses the catalyst chamber, and continues through the second pair of absorption trays and so on through the bottom set of absorption trays. Each tower of the Trail plant contains 13 catalytic sections and 14 absorption sections.

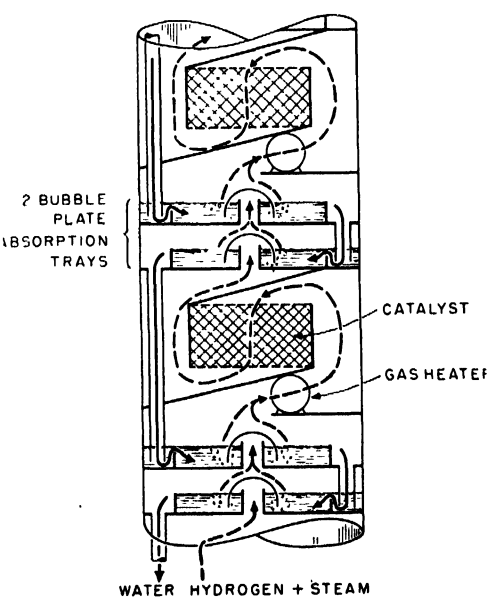

Figure 13. Section of exchange tower of Trail plant

In the gas flowing up through a catalyst chamber, deuterium is partially transferred from HD to HDO; as the gas next flows up through an absorption section, the HDO is partially absorbed from the gas phase by the downflowing water. The overall result is a transfer of deuterium from gas to liquid, so that as the gas flows up it is progressively depleted in HD, and as the liquid flows down it is progressively enriched in HDO.

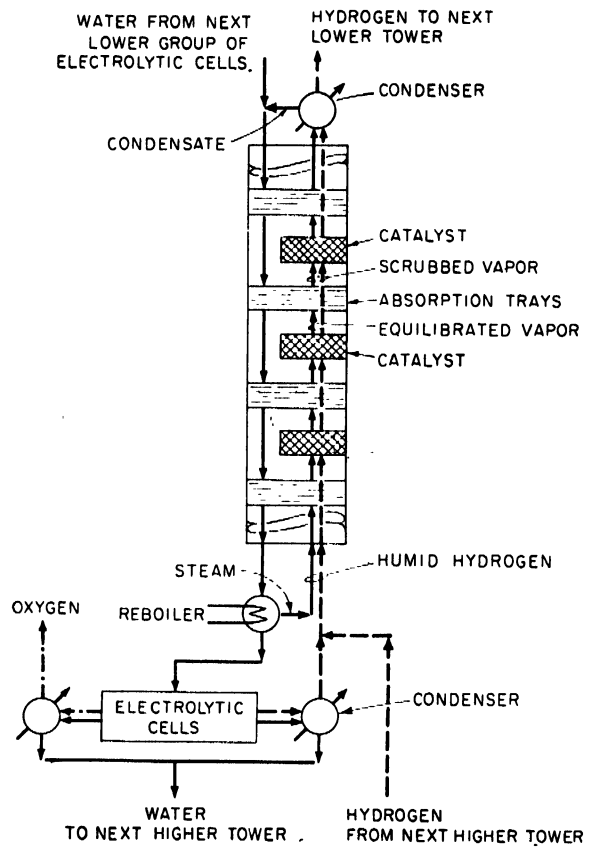

Figure 14. Flowsheet for one exchange tower and electrolytic cell group

Steam is produced and condensed only once for an entire tower, and the ratio of steam to hydrogen may be varied at will and is less than unity. Steam consumption is therefore only a small fraction of that of Fig. 12, but more catalytic stages are required for a given change in deuterium content.

The primary heavy-water plant at Trail consists of four groups of exchange towers and electrolytic cells connected in countercurrent cascade. Fig. 14 shows the flow through one such group. At the top of the tower, vapor is cooled in a condenser; most of the steam is condensed and combined with water from the next lower group of electrolytic cells. Hydrogen from the condenser is returned to the next lower group of towers. At the bottom of the tower steam is generated by vaporizing part of the water in a reboiler; hydrogen is generated by dissociating part of the water in a group of electrolytic cells with diaphragms to separate hydrogen from oxygen. Upflowing vapor consists of this steam and hydrogen, together with hydrogen from the next higher tower. Water fed forward to the next higher tower is obtained as condensate from the hydrogen and oxygen gases leaving the electrolytic cells. The forward feed is re-evaporated (not shown) to keep entrained electrolyte out of the towers.

6.32 Plant Flowsheet

Figure 15 shows how the electrolytic cells and exchange towers of the primary Trail plant are connected in countercurrent cascade. Flow rates and compositions are external to the towers; condensate and reboil steam quantities within the exchange towers have not been shown. Since these are observed quantities reported for the Trail plant,[16] they are not in exact material balance.

The main flow pattern is shown at the right of the figure. Water flowing down through the first exchange tower T-1 is enriched from a feed concentration of 0.0138 atom % D* to 0.037% D. Most of this water is electrolyzed in the first group of cells, C-1, where its D content is further increased to around 0.08%. The water is enriched to 0.143% D in the second column, and to 0.285% D in the second group of electrolytic cells, C-2, where about ¾ of the water is converted to hydrogen. By proceeding in this way through the third and fourth stages of towers and cells, the D content of the water is increased to 2.14%. Meanwhile the D content of the hydrogen, flowing countercurrent to the water, is decreased from 0.69% in the gas leaving the fourth group of cells, C-4, to 0.005% in the stripped hydrogen discharged from the plant.

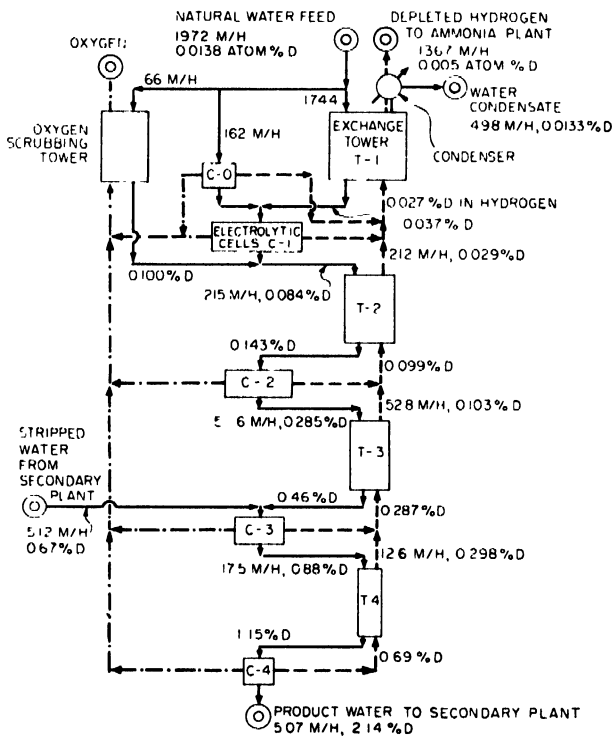

Figure 15. Flow external to towers of exchange plant at Trail

Table X. Equipment of Trail Exchange Plant

Stage	1	2	3	4
Number of electrolytic cells	2693 *	378	96	30
Number of exchange towers	3 †	1	1	1
Tower diameter, ft	8.5	5	2.5	1.5
Tower height, ft	112	108	97	96.5
Number of absorber plates	35 ‡	32 §	32 §	32 §
Number of catalyst chambers	13	13	13	13
Absorber plate spacing, in.	8	8	8	8
Catalyst depth, in.				
Provided	24	24	24	26
Used	4.5	6	6	4.25
Catalyst volume used, ft³	480	111	27	5.4
Catalyst type	Pt	Pt	Pt	Ni-Cr
Reboiler duty, BTU/hr				
Design	10,000,000	3,250,000	850,000	250,000
Operation	2,250,000	580,000	187,000	18,700
Condenser duty, BTU/hr				
Design	11,800,000	3,800,000	950,000	240,000
Operation	4,240,000	1,160,000	216,000	58,300

* 288 of these cells are in Group O.
† One spare.
‡ Six below bottom catalyst bed and five above top.
§ Six below bottom catalyst bed and two above top.

Superimposed on this main flow pattern are the following additional features:

1. Stripped water from the secondary plant containing 0.67% D is fed to stage 3 electrolytic cells.

2. Condensate from the top of the first tower containing 0.0133% D, slightly less than natural water, is wasted rather than being returned to this tower.

3. Some partially enriched water is carried with the oxygen leaving the cell gas coolers. These oxygen streams, at the left of Fig. 15, are combined and scrubbed with natural water, which is thereby enriched to 0.1% D. This water bypasses the first stage altogether.

4. Some feed water bypasses the first stage tower in order to feed a group of electrolytic cells C-0. These cells could not be made completely leakproof, and it was better to have the losses at the lowest possible D content. Water from C-0 is fed into the first-stage electrolytic cells, C-1, and hydrogen from C-0 is combined with hydrogen from C-1.

The reason for electrolyzing water at four different D contents rather than only at the rich end of the plant is that the amount of hydrogen needed for reflux becomes smaller as the water becomes more enriched. In this way, by electrolyzing most of the water ahead of the second stage, the amount of liquid and gas to be handled in the second stage is reduced, and the tower and reboiler of this stage can be made smaller and cheaper. Further, the deuterium holdup at higher enrichment is smaller, so that the plant takes less time to come to steady concentrations. This principle is important in all isotope separation processes and is especially important in this one because of its relatively large holdup per unit capacity.

*It is interesting that the D content of natural water at Trail is appreciably lower than the normal natural value of 0.0149%.

6.33 Stage Data

Table X summarizes data on the progressively smaller equipment used in the four stages of this exchange plant. The plant uses only 6 towers, of which one is a spare, to produce twice as much heavy water as the Morgantown water distillation plant, with 18 columns. As this table shows, the plant was overdesigned in respect to the reactor volume provided for catalyst and the steam generating and condensing capacity provided.

Table XI lists the principal operating conditions used in the exchange towers. Flow data are not entirely consistent with Fig. 15. The towers are operated at temperatures between 60 and 73°C, a condition found by experience to give maximum recovery. Lower temperature has the disadvantage that the amount of steam carried by the upflowing hydrogen is too small to transfer much deuterium from HD to HDO as the vapor flows up through a catalyst chamber. (As an extreme example, if the hydrogen carried no steam, there would be no enrichment.) Higher temperature has the disadvantage that the hydrogen carries so much excess steam that the change in HDO content of the vapor flowing through a catalyst chamber is small. (As an extreme example, at the normal boiling temperature, the tower would behave like a water distillation column, and the catalyst would have no effect.) Also, at higher temperature, the equilibrium constant is lower. At temperatures around 60–75°C, the enrichment per catalyst stage is a maximum. Somewhat higher temperatures are used in the first tower than in the others because the pressure there is higher.

As this table shows, both the platinum and nickel catalyst were very active. Despite the high space velocities used, a 95% approach to exchange equilibrium was attained in each catalyst bed, with fresh catalyst. After two years' operation, conversions were still in the range of 80% to 95%. Both catalyst

types are poisoned by KOH, CO or sulfur compounds, and can be used only with very pure hydrogen.

6.34 Costs

Capital costs for this plant, built in 1943, were:

	$
Plant (including CM&S revisions)	2,349,000
Research and development	472,200
Operating costs during 6 months to come to equilibrium	180,000
Total	3,001,200

Operating costs in 1945 were $30,000 per month, of which utilities were only $9000. At a production rate of 1100 pounds per month, unit costs in 1945 were: investment $227/lb D_2O/yr; operating $27.3/lb D_2O. Present operating costs[19] are $60/lb D_2O, including overhead and profit to CM&S.

6.35 Material Balance

The material balance for the conditions of Fig. 15 is:

	Moles/hr	*% D*	*Moles D_2/hr*
1. Feed	1972	0.0138	0.272
2. Water from sec. plant	5.12	0.67	0.0343
Input	1977		0.306
3. Product	5.07	2.14	0.1085
4. Waste condensate	498	0.0133	0.0663
5. Stripped hydrogen	1367	0.0050	0.0684
Output	1870		0.2432

There is evidently considerable loss at D enrichments above normal.

The net production is item 3 less item 2, or 0.0742 moles per hr, which is 1070 pounds D_2O per month. The net recovery due to exchange is the net production divided by the deuterium content of water converted to hydrogen:

$$\text{Net recovery} = \frac{0.0742}{1367 \times 0.000138} = 0.393 \qquad (6.1)$$

If there were no losses, the net recovery with hydrogen carrying 0.005% D from the plant would be

$$\frac{0.000138 - 0.000050}{0.000138} = 0.637 \qquad (6.2)$$

Table XI. Tower Operating Conditions, Trail Plant

Stage	*1*	*2*	*3*	*4*
Tower pressure, mm				
Top	833	716	798	713
Bottom	957	798	798	764
Average catalyst temp., °C	73	67	64	62
Average absorber temp., °C	69	64	61	60
Moles per hour				
Water, down	1667	275	68.6	20.28
Hydrogen, up	1369	212	52.8	12.6
Steam, up	466	66	13.8	3.18
Vapor velocity through Absorber plates (Murphree)	1.74	1.73	1.45	1.11
Space velocity through Catalyst (fresh) $H_2/ft^3/hr$	13,300	8800	8200	10,800
% approach to equilibrium				
absorber plates (Murphree)	53	37	48	38
catalyst (fresh)	95	95	95	95

This is almost as high as the maximum theoretical recovery, which is secured when the outgoing hydrogen is in exchange equilibrium with incoming liquid water feed. At 73°C, the catalyst temperature in the first stage tower, the equilibrium constant, K', for the reaction

$$H_2O\ (l) + HD\ (g) \rightleftharpoons HDO\ (l) + H_2\ (g)$$

is

$$K' = K\alpha^* = 2.92 \times 1.038 = 3.03 \qquad (6.3)$$

The minimum deuterium content possible for the outgoing hydrogen is

$$y_{min} = x_{feed}/K' = 0.000138/3.03 = 0.0000455 \qquad (6.4)$$

The maximum recovery possible is

$$\frac{0.000138 - 0.0000455}{0.000138} = 0.670 \qquad (6.5)$$

Thus, this plant does an efficient job of absorbing deuterium from hydrogen; its low recovery is due to losses rather than to failure to remove deuterium from the hydrogen treated. Most of the losses were in the electrolytic cells, which were not designed to minimize losses of water vapor.

6.4 Discussion of Electrolysis and Exchange Process

Operation of the Trail plant for over ten years has shown this process to be a feasible and relatively economic process for making heavy water. Most of the deficiencies of the Trail plant have been caused by the necessity of adapting an existing electrolytic plant to the production of heavy water by exchange. If a new electrolytic plant were to be built, it should be possible to design the electrolytic plant and associated exchange facilities to fit together more efficiently than was possible at Trail.

The following points are suggested for consideration in the design of a future electrolytic-and-exchange plant: 1. Losses of water and hydrogen should be minimized; 2. Electrolytic cells with maximum isotope-separation factor and minimum holdup should be developed; 3. The relative flow rates of water and hydrogen to each exchange tower should be so proportioned that every catalyst bed converts the same fraction of HD fed to it to HDO. In this way, the most efficient possible use is made of catalyst. This condition requires that there be no net transport of deuterium through an exchange column, or that

$$Gy = Lx \qquad (6.6)$$

where y is the atom fraction of deuterium in hydrogen, x is the atom fraction of deuterium in water, L is the downflow of water, and G is the upflow of hydrogen in the stream at top or bottom of a column. Since the entire net transport of deuterium was taken through the towers of the Trail plant, this condition was not realized there, with the result that the catalyst beds at the top of each tower converted a much smaller proportion of HD than those at the bottom.

If it should be possible to develop an electrolytic cell with an isotope separation factor in the neighborhood of 7, the above condition could be satisfied by a flowsheet like Fig. 16.

To illustrate the principle, complications introduced by feed of partially enriched water from the secondary plant and the oxygen-scrubbing tower have been omitted.

Figure 16 refers to production of hydrogen at the same rate as the Trail plant, 1367 moles per hour; enriched-water product has the same deuterium content as water from the Trail primary plant, 2.14 atom % D. This flowsheet represents what is thought to be the best that could be done in any future attempts to improve this process.

This flowsheet has been so arranged that:

1. There is no net transport of deuterium through the exchange towers.

2. At each mixing point the deuterium content of both streams is the same.

3. Each group of electrolytic cells and each exchange tower spans the same ratio of deuterium atom fractions. This ratio has been so chosen that the number of plates provided in the towers of the Trail plant would be sufficient for the conditions of Fig. 16.

Comparison with Fig. 15 shows that the main differences between this flow scheme and that of the Trail plant are:

1. Hydrogen from group 0 of electrolytic cells is discharged from the plant without passing through stage 1 towers. When the electrolytic separation factor is 7, this is possible without sacrifice of deuterium recovery; it has the important advantage of reducing the vapor load in stage 1 towers to only 36% that in the Trail plant.

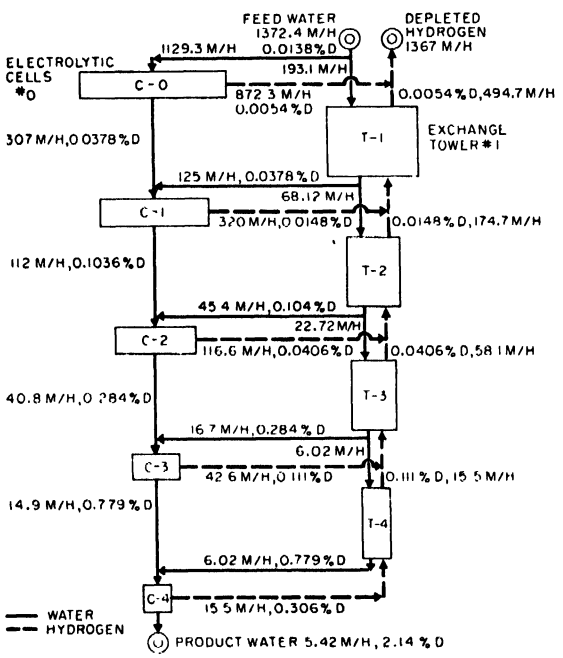

Figure 16. Cascade of exchange towers and electrolytic cells α (elect.) = 7

2. About 70% of the water fed to each stage bypasses the exchange tower; in the Trail plant all of the water flows through the exchange tower and electrolytic cell in series.

This idealized plant and the Trail plant are compared further in Table XII. The net production and the recovery of the idealized plant are greater by 56%, despite the somewhat higher D content of depleted hydrogen. This is because of the assumption that losses could be eliminated. The total hydrogen flow through the exchange towers of the idealized plant is only 45% that of the Trail plant, with most of the reduction in the first stage.

This comparison and the cost data on the Trail plant can be used to get a rough idea of the lowest value to which the cost of heavy water by the process could be reduced if the assumptions made for the idealized plant could be realized.

The production rate of the idealized plant is 20,000 pounds D_2O per year.

The initial cost of the plant is assumed to be proportional to the square root of the total hydrogen flow rate through the exchange columns. An allowance is made for increase in the construction-cost index since 1943 by a factor of 2.23. Development and startup costs for the Trail plant are not included. The initial cost of the idealized plant, built today, would be:

$$\$2{,}350{,}000 \times \sqrt{0.45} \times 2.23 = \$3{,}550{,}000$$

and the unit investment cost would be

$$\frac{3{,}550{,}000}{20{,}000} = \$178/\text{lb } D_2O/\text{yr}$$

Unit operating costs in the idealized plant are assumed to be the present unit operating cost divided by the ratio of production in the idealized plant to the present plant, or

$$60/1.56 = \$38/\text{lb}$$

6.5 Other Sources of Hydrogen

The steam-hydrogen exchange process, as now practiced, is restricted to hydrogen produced electrolytically, because the catalysts thus far developed are poisoned by CO, H_2S or other impurities in in-

Table XII. Comparison of Trail Plant and Idealized Electrolytic and Exchange Plant

Plant: / *Figure:*	*Trail* 15	*Idealized* 16	*Idealized* ÷ *Trail*
Separation factor in electrolysis	3	7	--
Net D_2O product, moles/hr	0.0742	0.116	1.56
Atom % D in depleted hydrogen	0.0050	0.0054	--
Net D_2O recovery, %	39%	61%	1.56
Hydrogen flow through exchange towers, moles/hr			
Stage 1	1367	494.7	0.36
Stage 2	212	174.7	0.82
Stage 3	52.8	58.1	1.12
Stage 4	12.6	15.5	1.23
Total	1644.4	743.0	0.45

dustrial hydrogen from other sources. Since there are few places in the world where it is economic to produce large amounts of hydrogen electrolytically, the total amount of heavy water which can be made by plants like Trail is limited. Development of catalysts which could be used with coke-oven gas, water gas, or ammonia synthesis gas made by reforming hydrocarbons would greatly increase the amount of heavy water which might be made by the simple steam-hydrogen exchange process.

7. DUAL-TEMPERATURE EXCHANGE PROCESSES

7.1 Steam-hydrogen Exchange

To free the steam-hydrogen exchange process from its dependence on hydrogen produced for other purposes, Harteck and Suess[6] proposed a modification in which hydrogen is recycled through two exchange reactors in series, one at low temperture and the other at high. The dependence of equilibrium constant for the reaction $H_2O + HD \rightleftarrows H_2 + HDO$ on temperature is given in Table IX.

Figure 17 is a simple example to show the principle of such a dual-temperature process. Since the equilibrium constant is around 2.8 at low temperatures and around 1.3 at high, deuterium will be transferred from hydrogen to steam in the cold reactor and from steam to hydrogen in the hot. The steam from the cold reactor is therefore enriched in deuterium content to 1.19 times feed and that

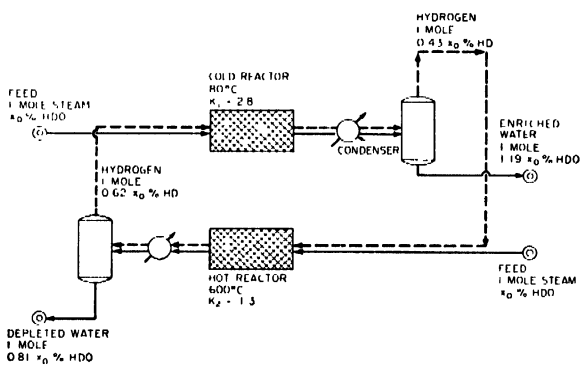

Figure 17. Principle of dual-temperature steam-hydrogen exchange process

from the hot reactor is depleted in deuterium content to 0.81 times feed. For the special case in which one mole of steam is fed to the hot reactor and one mole to the cold, for every mole of hydrogen circulated, the separation factor is $1.19/0.81 = 1.47$.

Like the simple exchange process of Fig. 12, steam consumption in the scheme of Fig. 17 is high. However, Trail-type exchange towers may be used to reduce the steam consumption in the dual-temperature process also. Cerrai *et al.*[2] have studied a number of possible flow schemes for the dual-temperature steam-hydrogen exchange process, and have shown that the one illustrated by Fig. 18 has the maximum possible separation factor.

Liquid water is enriched from x_0 to x' mole fraction HDO by flow down the enriching absorber.

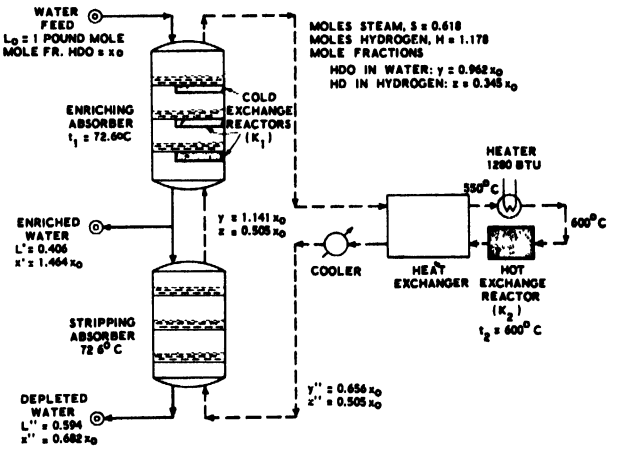

Figure 18. Stage of dual-temperature $H_2 - H_2O$ exchange process

This is a Trail-type exchange tower, at a low temperature t_1 in which absorption trays and exchange reactors alternate. Deuterium to enrich this water is obtained from the steam and hydrogen flowing up through this column. A fraction L' of the enriched water is drawn off as product. The remaining water is partially stripped of HDO by flow down the lower-stripping absorber. Stripping vapor for this absorber is obtained by recycling the mixture of hydrogen and steam from the top of the upper absorber through an exchange reactor at a high temperature, t_2, where the equilibrium constant is lower than at t_1. The hot exchange reactor transfers deuterium from HDO to HD, and thus provides stripping vapor depleted in HDO for the lower absorber, while at the same time making hydrogen enriched in HD which passes through the lower absorber unchanged and then helps transfer deuterium to water in the upper absorber. Water leaving the lower absorber has a lower HDO content (x'') than feed, because all of the deuterium added to the water in the upper absorber is taken from the smaller quantity of water flowing through the lower absorber, by means of the recycled hydrogen.

The particular conditions shown on this flowsheet are those which give maximum separation factor for a hot reactor temperature of 600°C and atmospheric pressure. The separation factor of $1.464/0.682 = 2.15$ is much higher than in the simpler scheme of Fig. 17 (1.47), and the process consumes no steam. The only heat input is that needed to make up the heat exchanger temperature difference, and this can be made as small as desired by providing sufficient heat transfer surface. In this example, a temperature difference of 50°C was assumed.

The higher the temperature t_2 the better the separation. Any catalysis in the heat exchanger while the gases are being cooled cancels some of the exchange achieved at the highest temperature.

To multiply the separation, stages may be connected in a recycle cascade, as shown in Fig. 19. For clarity, only the water flow is shown.

Cerrai *et al.*[2] have shown that the maximum separation factor for the flow scheme of Fig. 18 is

$$\alpha = \frac{K_1}{K_2} \tag{7.1}$$

where K_1 and K_2 are equilibrium constants for the exchange reaction at temperatures t_1 and t_2. To obtain this maximum separation factor, the following conditions must be met:

1. In gases leaving the hot reactor, exchange equilibrium must be attained.

2. In the lower, stripping absorber, flow rates of liquid (L'') and steam (S) must be so proportioned that HDO absorption equilibrium is maintained on all plates.

3. In the upper, enriching absorber, flow rates of liquid (L), steam (S) and hydrogen (H) must be so proportioned that deuterium exchange equilibrium between liquid and vapor is maintained on all plates.

Complete attainment of equilibrium would require an infinite volume of catalyst and an infinite number of plates in each tower. These conditions and the corresponding separation factor are therefore upper limits which may be approached, but not attained, in practice.

These three conditions are sufficient to determine the separation factor (α) and the flow rates of steam (S) and hydrogen (H), once the "cut" of the stage, L'/L_0, has been set. The optimum cut, in a cascade like Fig. 19, is that which results in equal compositions for the streams that come together at each mixing point.

Equal compositions at mixing points are secured when

$$\frac{x'}{x_0} = \frac{x_0}{x''} = \sqrt{\alpha} \tag{7.2}$$

By material balance

$$\frac{L'}{L_0}x' + \left(1 - \frac{L'}{L_0}\right)x'' = x_0 \tag{7.3}$$

When the mole fractions are eliminated from these three equations, there results

Cut:

$$L'/L_0 = 1/(\sqrt{\alpha} + 1) \tag{7.4}$$

By application of the requisite material balance and equilibrium relations to the two absorbers and the hot exchange reactor, it is found that

Separation Factor:

$$\alpha = K_1/K_2 \tag{7.5}$$

Steam:

$$S/L_0 = \frac{\alpha^* \sqrt{K_1/K_2}}{\sqrt{K_1/K_2} + 1} \tag{7.6}$$

Hydrogen:

$$H/L_0 = \frac{\alpha^* K_1}{\sqrt{K_1/K_2} + 1} \tag{7.7}$$

Here, α^* is the relative volatility of H_2O relative to HDO;

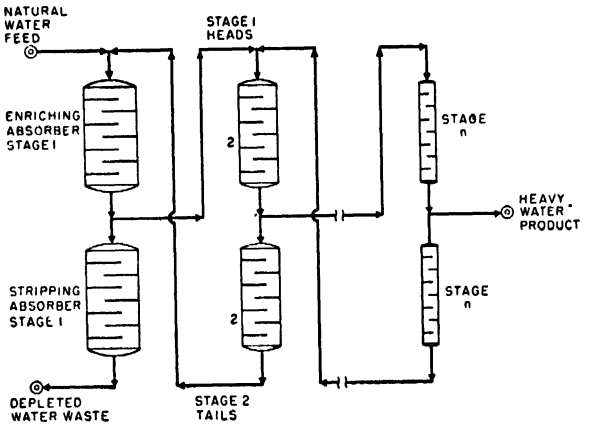

Figure 19. Flow of water through cascade of steam-hydrogen exchange stages

$$\alpha^* = x/y \tag{7.8}$$

These relations are valid when the deuterium content of water and hydrogen is less than a few per cent.

The temperature t_1 at which the absorbers must be run is that at which the vapor pressure of water π gives the desired ratio of S to II:

$$\frac{S}{S+H} = \frac{\pi}{P} \tag{7.9}$$

at the total pressure P. The quantities shown in Fig. 18 have been derived for a high temperature (t_2) of 600°C and a pressure of one atmosphere, for which the required low temperature (t_2) is 72.6°C. This is close to the temperature used at Trail.

Equilibrium constants for the temperatures of Fig. 18 are $\alpha^* = 1.039$, $K_2 = 2.79$, and $K_1 = 1.30$, so that $\alpha = K_2/K_1 = 2.15$.

For these flow quantities, the heat consumption is 1280 BTU per pound mole of stage feed.

It is of interest to evaluate the number of stages, the total amount of hydrogen circulated, and total heat input per pound of D_2O produced for a dual-temperature cascade like Fig. 19 enriching deuterium through the same range as the Trail plant, from $x_0 = 0.000138$ to $x_P = 0.0214$. The number of stages is given by (5.5):

$$n = 2\frac{\log\left[\dfrac{0.0214}{0.9786}\cdot\dfrac{0.999862}{0.000138}\right]}{\log 2.15} = 13.2 \tag{7.10}$$

This may be compared with 4 stages at Trail.

The sum of the stage feed rates for a cascade producing one mole of D_2O is

$$\frac{\Sigma L}{P x_P} = \frac{1}{x_P}\frac{\sqrt{\alpha}+1}{\sqrt{\alpha}-1}\left[\frac{\sqrt{\alpha}}{\sqrt{\alpha}-1} \times \left(\frac{x_P}{x_0} - 1\right) - n\right] = 118{,}700 \tag{7.11}$$

This equation, derived from the general theory of isotope separation for the case x_0, $x_P << 1$, is given by Cerrai *et al.*[2] The total amount of hydrogen circulated per mole D_2O is

$$\frac{\Sigma L}{P.x_P} \times \frac{H}{L_0} = 118{,}700 \times 1.178 = 140{,}000 \quad (7.12)$$

This may be compared with 1644.4/0.0742 = 22,200 at Trail, obtained from Table XII. These two results suggest that the capital investment for a dual-temperature steam-hydrogen exchange plant using Trail-type towers would be rather high.

The heat consumption of this process is strikingly low, however. The heat input is only

$$\frac{118{,}700 \times 1280}{20} = 7{,}600{,}000 \text{ BTU/lb } D_2O \quad (7.13)$$

At \$0.20 per million BTU, the cost of this heat would be only \$1.52 per pound D_2O. Although these are idealized, minimum figures, it is evident that the dual-temperature exchange process permits notable economies in energy consumption. By comparison, the cost of steam in water distillation was found to be \$26.7 per pound D_2O.

The large number of stages, and the probable high capital cost, of the steam-hydrogen exchange plant just described is caused as much as anything by the fact that only one exchange equilibrium contact at the high temperature is obtained per stage. This limits the separation per stage to K_2/K_1. Greater separation per stage could be obtained by using a Trail-type tower for both high and low temperature exchange reactors. The separation per stage could then be increased to any degree by using a sufficient number of equilibrium contacts in both towers. However, it would not be possible then to use the optimum ratio of steam to hydrogen in both towers, and the deuterium transfer capacity per catalyst contact would be reduced.

If it were possible to develop a catalyst for the steam-hydrogen exchange reaction which would not be inactivated by liquid water, the need for Trail-type towers would be eliminated and conventional bubble-plate or packed liquid-vapor contactors could be used. Nothing would improve the prospects for the dual-temperature steam-hydrogen exchange process more than discovery of such a catalyst.

7.2 Other Exchange Reactions

Table XIII lists the separation factor for exchange of deuterium between a number of pairs of compounds of hydrogen, one liquid and the other gaseous. The separation factor (α) has been obtained by multiplying the equilibrium constant (K) by the ratio of the number of hydrogen atoms in the gaseous compound to the number in the liquid compound. In a dual-temperature process, the ratio of the separation factor at the low temperature to that at the high temperature is an index of the ease of separation; the more this ratio departs from unity, the smaller the number of stages required and the smaller the total flow rate and heat requirement. The ratio of these factors at 25° and 100°C is given in the next-to-the-last column, and the reactions have been arranged in the order of increasing values of this ratio.

The first five of these reactions proceed rapidly in the liquid phase without catalysis. The ammonia-water reaction is the only one that does not present corrosion problems, but this has too poor a separation-factor ratio to be useful. The H_2S-water reaction has a ratio high enough for an operable process, but the solutions are corrosive. Each of the three halogen acid-water systems is very corrosive, and forms a constant boiling mixture which complicates design of a dual-temperature process.

The two best reactions, from the standpoint of separation-factor ratios, are ammonia-hydrogen and water-hydrogen. Neither system is corrosive. Unfortunately, both require catalysis.

Dual-temperature processes based on one or more of these reactions have been studied by the Manhattan District,[20] in the USA, and by Geib[6] of I. G. Farben in Germany. Geib proposed use of H_2S-water in the dual-temperature tower system shown in Fig. 20, operation at 10 atm. Natural liquid water feed is enriched in deuterium by flow counter to H_2S vapor through the cold tower, at 25°C. A portion of the enriched water leaving the cold tower is withdrawn as product, and the remainder is set through the hot tower at 100°C. Here the water is stripped of deuterium by counter-flowing H_2S vapor recycled from the top of the hot tower; this is possible because the separation factor for transfer of deuterium from H_2S to water is less favorable in the hot tower than in the cold.

Table XIII. Separation Factors in Liquid-Vapor Deuterium Exchange Reactions

Reactants		*Products*			*Separation factor (α)*					*Ratio*	
Liq.	*Gas*	*Liq.*	*Gas*	α/K	*0°C*	*25°C*	*100°C*	*125°C*	*227°C*	α_{25}/α_{100}	*Ref.*
H_2O	$+ NH_2D \rightleftharpoons$ HDO	$+ NH_3$		3/2	1.02	1.00	0.99	—	0.98	1.01	13
H_2O	$+ HDS \rightleftharpoons$ HDO	$+ H_2S$		1	2.52	2.34	1.92	—	—	1.22	6
H_2O	+ DCl $\rightleftharpoons$ HDO	+ HCl		1/2	2.87	2.51	1.98*	1.87	1.59	1.27	13,23
H_2O	+ DBr $\rightleftharpoons$ HDO	+ HBr		1/2	3.57	3.07	2.34*	2.17	1.79	1.31	13,23
H_2O	+ DI $\rightleftharpoons$ HDO	+ HI		1/2	4.55	3.80	2.78*	2.56	2.05	1.37	13,23
NH_3†	+ HD $\rightleftharpoons$ NH_2D†	$+ H_2$		2/3	4.56	3.88	2.73	—	—	1.42	13
H_2O	+ HD $\rightleftharpoons$ HDO	$+ H_2$		1	4.69	3.87	2.69	2.47	1.94	1.44	13,23

* Interpolated from reference 23.
† Gas phase.

Heat exchangers make possible recovery of some of the heat contained in streams leaving the hot tower. Because the exchange reaction in this system proceeds without catalysis, it should be possible to use ordinary bubble-plate towers.

The principle of this process is illustrated further by the McCabe-Thiele diagram, Fig. 21. The spread between the equilibrium lines, at 25°C and 100°C, is what makes separation possible. The slope of the operating line in the cold tower is F/S, the ratio of water feed rate to H_2S gas flow rate. The slope of the operating line in the hot tower is $(F\text{-}P)/S$, the ratio of water waste rate to H_2S gas flow rate; this is less than in the cold tower. Since the deuterium content of water between the two columns (x_P) and of H_2S between the two columns (y_P) is the same in each, both operating lines end at a common point at the top right. Since the deuterium content of H_2S leaving the top of the cold tower (y_F) is the same as that entering the bottom of the hot tower, the left end of both lines is at the same value of y. The number of plates in each tower determines the level of these lines, and from them the deuterium content of waste (x_W) and product (x_P).

As the number of plates is increased, the deuterium content of product can be increased to any desired degree. Thus, in this type of dual-temperature process, unlike Fig. 19, it would be possible to obtain full separation in a single stage. In practice, if a high degree of enrichment were desired, a series of pairs of hot and cold towers of decreasing size would be used, to reduce tower costs and holdup.

As the number of plates is increased, the lower ends of each operating line approach the corresponding equilibrium line. The maximum spread between

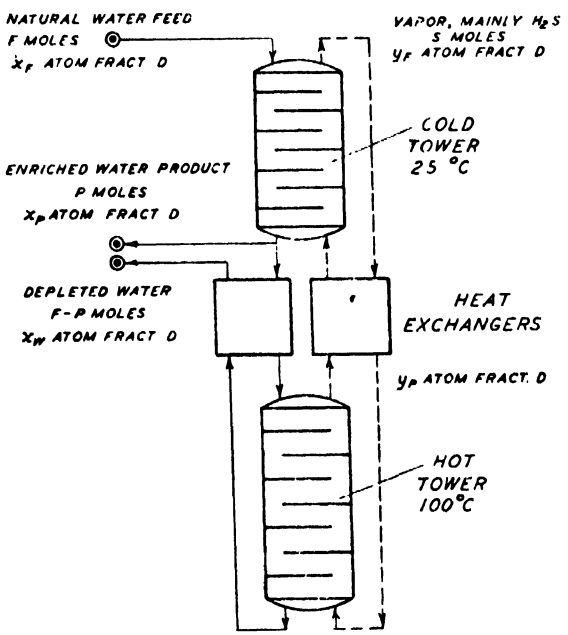

Figure 20. Dual-temperature steam-H_2S exchange process

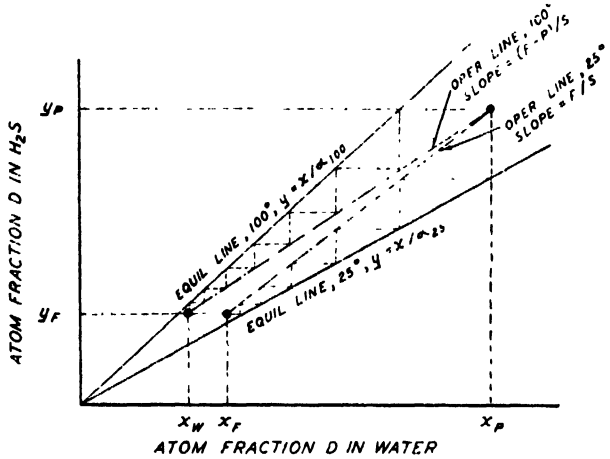

Figure 21. McCabe-Thiele diagram for dual-temperature steam-H_2S exchange process

x_W and x_F occurs with an infinite number of plates, at which

$$\frac{x_W}{x_F} = \frac{\alpha_{100}}{\alpha_{25}} \qquad (7.14)$$

since both points are on the same horizontal line.

When $x_P > < x_F$, some simple relations hold. The fractional recover of deuterium from feed is

$$1 - \frac{x_W}{x_F} = 1 - \frac{\alpha_{100}}{\alpha_{25}} = 0.18 \qquad (7.15)$$

The minimum ratio of feed water to product D_2O is

$$1/(x_F - x_W) = 1/0.18 \quad x_F = 37{,}300 \qquad (7.16)$$

The slope of both operating lines becomes nearly equal, and must lie between the slopes of the equilibrium lines:

$$\frac{1}{\alpha_{100}} > F/S \cong (F - P)/S > \frac{1}{\alpha_{25}} \qquad (7.17)$$

Thus the minimum ratio of H_2S to feed is

$$(S/F)_{min} = \alpha_{100} = 1.92 \qquad (7.18)$$

and the minimum ratio of H_2S to product D_2O is

$$1.92 \times 37{,}300 = 71{,}600 \qquad (7.19)$$

Although these flows are large, they are smaller than in the water-distillation process, or in the steam-hydrogen process of Fig. 18, so the plant should be smaller and less costly. Because of these large flow rates, efficient heat exchange is needed in a dual-temperature plant.

The dual-temperature water-H_2S process was considered by the Manhattan District in 1943, but no plant was built at that time because of anticipated corrosion difficulties. The process is now being used in the heavy-water plants of the U.S. Atomic Energy Commission, where the primary concentration of

deuterium is effected by this means. Heavy water is offered for sale at a price of $28 per pound.

A dual-temperature system using water, recycle ammonia and recycle hydrogen was also considered by the Manhattan District, but the absence of a catalyst for exchange between ammonia and hydrogen made the process too complex to be of interest. Subsequently, however, it has been found[4] that potassium amide, dissolved in liquid ammonia, catalyzed this reaction. This reopens the possibility of using the dual-temperature ammonia-hydrogen process. To free the plant from dependence on fresh ammonia or fresh hydrogen as a source of deuterium, depleted ammonia from the dual-temperature process could be run counter to fresh water in a water-ammonia exchange column, to re-enrich the ammonia in deuterium for recycle to the dual-temperature system.

If a practicable, liquid-phase catalyst could be found for the hydrogen-water exchange reaction, this system would provide the best dual-temperature process of all.

8. SUMMARY AND CONCLUSIONS

The most suitable process for production of deuterium in a particular situation will depend on the rate of production required and on availability of low-cost energy sources or favorable feed situations.

Unless at least several tons per year of heavy water are to be produced for a period of ten years or more, it would not pay to build and operate a heavy-water plant; the cost of producing on a small scale or for a short time is much higher than for the large-scale, long-term producer.

Where ammonia synthesis gas or water gas containing at least 20-million cubic feet of hydrogen per day is being produced, the hydrogen-distillation process has promise of producing heavy water at lower cost than any of the other processes. This is particularly true of gas for ammonia synthesis purified by washing out impurities with liquid nitrogen. Where heat is very cheap, and there is a market for large blocks of electric power, distillation of water using low-pressure exhaust steam from a power plant has possible application.

Where electrolytic hydrogen can be produced for 50 cents per thousand cubic feet or less, the electrolysis of water or the steam-hydrogen exchange process used at Trail have possible application.

In all of these processes, heavy water is the by-product of another operation which carries the major part of the costs; these by-product processes have an economic advantage over single-purpose processes whose sole product is heavy water. However, since the heavy-water production rate of by-product processes is limited by the rate at which the main product is made, none of these by-product processes will produce enough heavy water for a large nuclear power industry. For production of heavy water at rates in excess of 40 tons per year, single-purpose processes are required, of which the following merit consideration: (1) distillation of water, using vapor recompression to reboil tower bottoms; (2) distillation of hydrogen supplied with deuterium by exchange with steam at high temperature; (3) exchange between steam and hydrogen sulfide at two temperatures; and (4) exchange between steam and hydrogen at two temperatures.

Table XIV. By-product Heavy-Water Processes

Process	*Distillation of ammonia synthesis gas*	*Distillation of water with low-pressure by-product steam*	*Electrolysis of water*	*Electrolysis of water plus exchange of hydrogen with steam*
Main product made per pound D_2O	H_2: 162 MCF* or NH_3: 2.2T	10,800 kwh	H_2: 390 MCF or NH_3: 5.2T	H_2: 224 MCF or NH_3: 3.0T
Separation factor	1.39	1.05	7	7, 2.8
Deuterium recovery	86%	3.9%	33%	61%
Moles vapor processed per mole D_2O produced	34,700	198,000	21,400	18,200
Energy input per pound D_2O	1690 kwh	178,000 lb 22 psia steam	57,800 kwh	31,800 kwh
Unit costs				
Plant, \$/lb D_2O/yr	170	155	?	178
Operation, \$/lb D_2O	16	34	?	38
Total, plant charged at 5%/yr, \$/lb D_2O	24	42	?	47
Cost assumptions	Nat. gas at 10¢/MCF*	High press. steam at 40¢ 1000 lb	H_2 made for 50¢/MCF	—
Engineering problems	Handling large amounts of liquid H_2	None	Development of electrolytic cell with high separation factor	

* MCF stands for 1000 ft.^{3} of gas at 60°F and 1 atm.
† T stands for one short ton, 2000 lb.

8.1 By-product Processes

Table XIV summarizes information on the four by-product processes which have been described in this paper. To provide a common basis for cost comparisons a total cost for each process has been computed from the unit operating cost and the unit plant cost, with changes against plant investment at 5%/yr as is illustrative of a government-financed venture.

Except for the electrolysis of water, the distillation of ammonia synthesis gas has the lowest operating cost of all the processes listed, $16 per pound, and the lowest total cost, $24 per pound. Its energy demand is by far the lowest, 1690 kwh per pound, and the unit investment cost is of the same order as the other processes. It realizes these advantages, however, only in large-size plants, handling 20-million cubic feet of hydrogen per day or more. However, operating conditions are extreme, and handling of liquid hydrogen on so large a scale is without precedent. Nevertheless, it is believed that the low-temperature engineering problems can be solved, and that this process represents the cheapest way of producing deuterium at rates of from 20 to 40 tons of heavy water per year. The upper limit is set by the maximum hydrogen-productive capacity now available at any one place.

Distillation of water using by-product, low-pressure exhaust steam can be practiced wherever fuel is cheap and where there is need for a large block of electric power. Although the cost is higher than in hydrogen distillation, operating conditions are mild, and there are no novel engineering problems. A 100,000-kw steam-power plant which made its steam for 40 cents per thousand pounds would produce 40 tons of heavy water per year at a total cost of around $50 per pound. There is a possibility of reducing the cost by developing even better tower internals than Spraypak.

At the few places in the world where electrolytic hydrogen can be made for 50 cents per thousand cubic feet or less, by-product production of heavy water is economically sound. The sacrifice in hydrogen production incurred to make heavy water need not contribute more than $13 per pound to the cost of heavy water, though the need for efficient condensers to recover partially enriched water from hydrogen and oxygen, and the complications of connecting cells in series cascade would add something to the cost. The amount of heavy water that can be made this way is small, however. Even if the separation factor could be increased to 7, at a large plant making 500,000 ft^3 of hydrogen per hour only 5 tons of heavy water per year could be made by electrolysis alone.

Addition of steam-hydrogen exchange facilities to an electrolytic heavy-water plant would almost double the amount of heavy water which might be recovered, though apparently not without an increase in cost. This process, too, is of limited applicability so long as it is dependent on electrolytic hydrogen. If a catalyst which would not be poisoned by ammonia synthesis gas or other abundant hydrogen-rich gases could be developed, the steam-hydrogen exchange process would become much more attractive. Larger volumes of hydrogen would be available for processing, and unit costs could be reduced.

8.2 Single-Purpose Processes

None of the by-product processes will produce enough heavy water to fill many power reactors, which typically need a charge of 0.5 to 1 ton of heavy water per megawatt of electric output. For a large nuclear power industry, it will therefore be necessary to call on one or more of the single-purpose processes. Table XV summarizes information on four of the more promising of these processes which can be derived from the cases studied in this paper.

These processes have not been considered as fully as the by-product processes, and information on them is either a crude estimate or a theoretical limit.

Table XV. Single-Purpose Heavy-Water Processes

Process	*Distillation of hydrogen fed deuterium by exchange with steam*	*Distillation of water with vapor recompression*	*Dual-temperature H_2S-water exchange*	*Dual-temperature steam-hydrogen exchange (Single hot contact per stage)*
Separation factor	1.39	1.05	1.22	<2.15
Deuterium recovery	13%	3.9%	<18%	<32%
Moles vapor processed per mole D_2O produced	108,000	198,000	>72,000	>203,000
Energy input per pound D_2O	~2300 kwh, plus heat for exchange system	~10,000 kwh	small	>2230 kwh
Engineering problems	Handling large amounts of liquid hydrogen; prevention of steam-hydrogen reaction in heat exchanger	None	Corrosion	Prevention of steam-hydrogen reaction in heat exchanger

Consequently, no cost data are included in Table XI. All of these processes use water as primary feed, and hence are unlimited in potential capacity.

Production of deuterium by distillation of hydrogen supplied with deuterium through exchange with steam will cost more than distillation of ammonia synthesis gas. The addition of high-temperature exchange equipment adds to the cost of the plant. Hydrogen entering the low-temperature plant will carry only around 0.01% D instead of the 0.0136% D in ammonia synthesis gas; for a given product rate, the low-temperature plant is therefore bigger, and its power demand is greater. Heat must also be provided for the exchange system.

Distillation of water with vapor recompression will cost more than with low-pressure by-product steam, because of the additional investment in compressors and the need to supply energy as work rather than as low-level heat. The power demand of around 10,000 kwh per pound of heavy water practically rules this process out, unless tower packing with lower pressure drop per theoretical plate can be developed.

The dual-temperature H_2S-water exchange process has the advantages of smaller amounts of gas to be handled and lower energy demand than distillation of water, but corrosion is a problem. Where high production rates are wanted, this is a dependable, low-cost process.

The form of the dual-temperature steam-hydrogen exchange process examined in Section 7, with only one equilibrium contact per stage at high temperature, appears to use too much plant for low-cost production, even though its energy demand is very low. Alternative schemes using simpler equipment at the expense of greater energy consumption might make this process look more favorable. Development of a cheap catalyst for this reaction which would permit use of conventional absorption towers would completely change the picture for this process and would make the dual-temperature, steam-hydrogen exchange process the most economic of all the single-purpose heavy-water processes.

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The Design of Isotope Separation Plants: Some Basic Design Equations for the Distillation Process

By I. Dostrovsky and Y. Lehrer,* Israel

Various countercurrent processes have been used for the separation of isotopes. Starting from the simple differential equations which describe such processes it is possible to develop a complete mathematical analysis of practical plants. Several such analyses have already been reported.[1-3]

In the present paper the solutions of the differential equations are presented in a form which is particularly useful in the design of plants for the production of heavy water by fractional distillation.

Starting with the basic differential equations for the steady state[2,3]

$$L\frac{dN}{dz} + kA(N - \alpha n) = 0$$

$$\frac{dn}{dz} + kA(N - \alpha n) = 0 \qquad \text{For dilute range.} \quad (1)$$

where L, l are flow rates of liquid and vapour, α is the unit process separation factor defined here from the equation: $N/(1-N) = \alpha n/(1-n)$, and k is an isotope-transfer coefficient defined as quantity per unit time per unit volume of packing.

and dividing by L and l and substituting the variable $\zeta = z/Z$ we obtain:

$$\frac{dN}{d\zeta} + \frac{kAZ}{L}(N - \alpha n) = 0$$

$$\frac{dN}{d\zeta} + \frac{kAZ}{l}(N - \alpha n) = 0 \qquad (2)$$

These equations may be solved readily to give:

$$\frac{d(N - \alpha n)}{d\zeta} = \Omega(N - \alpha n) \qquad (3)$$

where

$$\Omega = \frac{kAZ}{L}\,\frac{(\alpha L - l)}{l} = \frac{kV}{L} \times \frac{\alpha L - l}{l}$$

and hence:

$$N(\zeta) - \alpha n(\zeta) = [N(0) - \alpha n(0)]e^{\Omega\zeta} \qquad (4)$$

$$e^{\Omega} = \frac{N(1) - \alpha n(1)}{N(0) - \alpha n(0)}$$

Further development can only be made by reference to the boundary conditions.

Consider any cascade of which the unit under discussion is a part, such as Fig. 1.

Considering the material balance:

$$L_s - l_s = P$$
$$L_s N_s(0) - l_s n_s(0) = P N_p$$
$$L_s N_s(1) - l_s n_s(1) = P N_p \qquad (5)$$

Equation 4 takes the form:

$$e^{\Omega} = \frac{l_s - \frac{\alpha}{\alpha - 1}\left(\frac{Q_p}{Q_s} - 1\right)P}{l_s - \frac{\alpha}{\alpha - 1}(Q_p - 1)P} Q_s \qquad (6)$$

Since e^{Ω} must always be greater than 1 (i.e., $\Omega > 0$),

$$l_s \geqslant \frac{\alpha P(Q_p - 1)}{\alpha - 1}$$

we define $$l_{s_{min}} = \frac{\alpha P(Q_p - 1)}{\alpha - 1} \qquad (7)$$

This equation gives us immediately the minimum flow required in each stage of a cascade (for infinite efficiency of the stage). The same result may be obtained directly from considerations of mass balance.

Since the smallest value of $n(0)$ is $N(0)/\alpha$

we have: $(l + P)N_0 - n(0) = PN_p$

and since $N(0)/\alpha \leqslant n(0) \leqslant N(0)$

$$l = P(N_p - N_0)/[N(0) - n(0)]$$

maximum isotope transport occurs when $n(0) = N(0)/\alpha$ and, therefore, the value of l is then at a minimum, and is given by

$$l_{min} = \frac{\alpha P(Q - 1)}{\alpha - 1}$$

the same result as was obtained in Equation 7.

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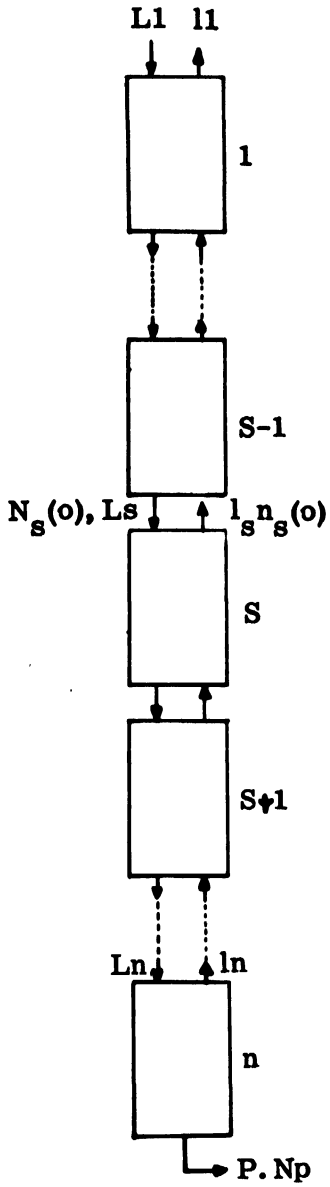

Figure 1

Substituting this value of $l_{s_{min}}$ in Equation 6 and ntroducing $l_s = \frac{l}{l_{s_{min}}}$ we obtain:

$$e\Omega = \frac{Q_s\left[l_s - \dfrac{Q_p - Q_s}{Q_s(Q_p - 1)}\right]}{l_s - 1} \qquad (8)$$

$$e^{\Omega} = \ln \frac{l_s Q_s - \dfrac{Q_p - Q_s}{Q_p - 1}}{l_s - 1} \qquad (9)$$

$$\frac{kV}{L_s} = \frac{l_s}{L_s - l_s} \ln \frac{l_s L_s - \dfrac{Q_p - Q_s}{Q_p - 1}}{l_s - 1} \qquad (10)$$

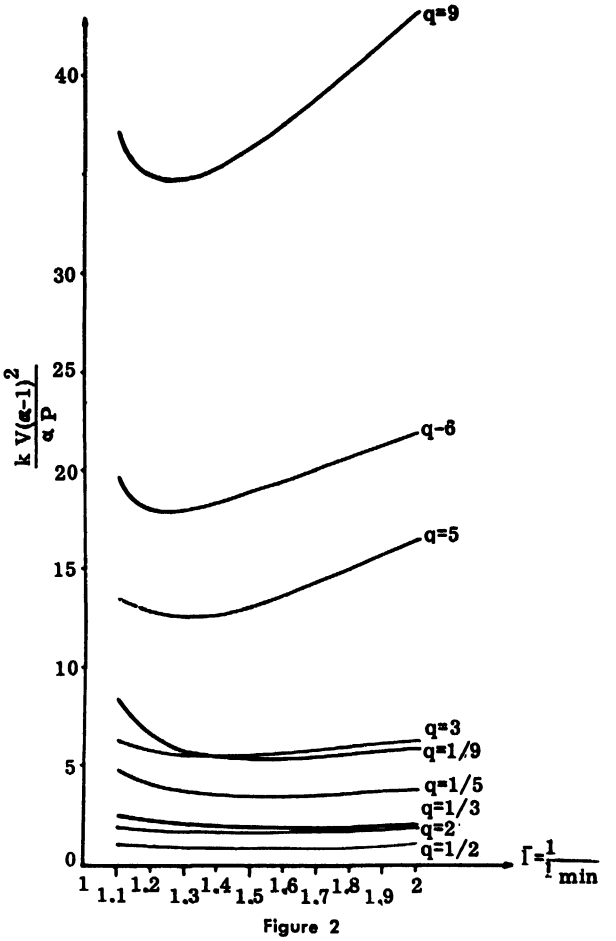

Figure 2

Equation 10 may be expressed as:

$$V = \frac{\alpha P}{k(\alpha - 1)^2} U(\alpha, Q_p, Q_s/l_s)$$

where

$$U(1, Q_p, Q_s/l_s)$$

$$= U(1, Q_p, Q_s/l_s)[1 + (\alpha - 1)/\alpha l_s(Q_p - 1)] \qquad (11)$$

$$U(\alpha, Q_p, Q_s/l_s)$$

$$= \frac{(Q_p - 1)l_s^2}{l_s + 1/(Q_p - 1)} \ln \frac{Q_s l_s - \dfrac{Q_p - Q_s}{Q_p - 1}}{l_s - 1}$$

Equation 11 describes equally well stripping cascades ($Q < 1$) provided production is taken as a negative quantity. This equation permits us to calculate the volume of packing needed in each stage of a cascade once the final enrichment has been determined. The function $U(\alpha, Q_p, Q_s/l_s)$ is almost independent of α and, therefore, the function $U(1, Q_p, Q_s/l_s)$ may be used. This function plotted against l_s is shown in Figs. 2 and 3.

The plot has a definite minimum, giving the least amount of packing required for the operation. The minimum occurs at values of l_s between 1.2 – 1.4; the plot of l_s for minimum volume as a function of Q_p is shown in Fig. 4. It is seen that for Q greater

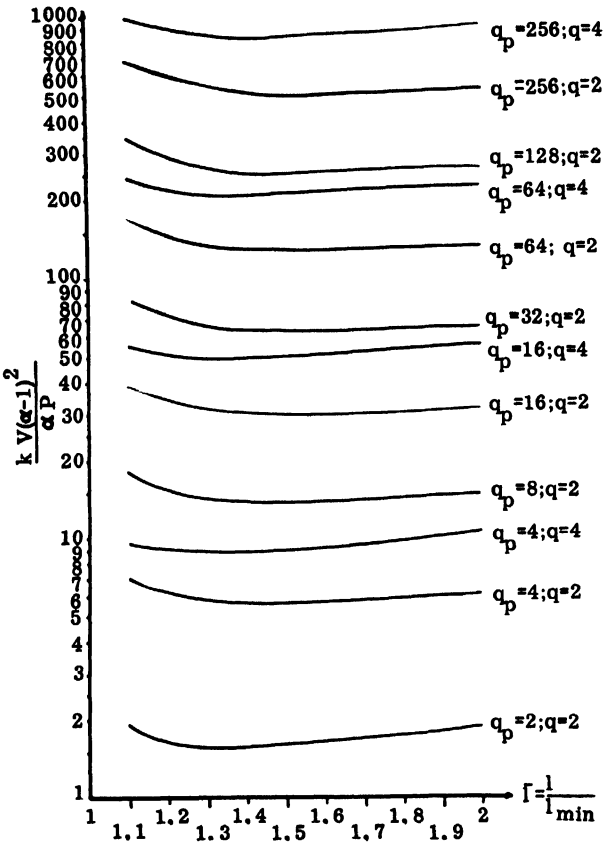

Figure 3

than about 4, l_{min} does not change much. For rapid calculation one can choose a value of l of 1.25. The actual flow through each stage can then be rapidly calculated. It should be emphasized that in any actual design we are interested in the part of the curve to the left of the minimum. To the right of this point both investment and energy increase. To the left of the minimum investment in column is increased while investment in heat-transfer elements and energy consumption decrease. We may set up an equation representing cost of product as follows:

$$\text{Cost} = aV + bL + cL$$

The first term represents the part of the cost due to investment in packing. The second term represents the part due to investment in heat-transfer components (boilers, condensers, etc.), while the third term represents energy expenditure per unit product. Curves may be drawn of this equation using various values of the coefficients a, b, c and the minimum will determine the optimal design. In general, the minimum of this curve will be somewhat to the left of the minimum in the plot of volume against flow.

The volume of the whole cascade may be obtained by summation of the minimum volumes of the individual stages. The dependence of this total volume upon the number of stages is shown in Fig. 5. The volume of the ideal cascade calculated from the equation:

$$\frac{kV(\alpha-1)^2}{P} = \frac{Q-1}{\frac{\alpha\eta}{\alpha-1}\left(1-\frac{\alpha\eta}{\alpha-1}\right)} - \frac{(\alpha-1)(1-\eta)}{1-\frac{\alpha\eta}{\alpha-1}} \times \ln\frac{1-\eta}{\frac{\alpha Q-1}{\alpha}\left(\frac{\alpha Q}{\alpha Q-1}-\frac{\alpha}{\alpha-1}\right)} \qquad (12)$$

where $\eta = PN_p/L_0N_0$ is also shown. It is seen that not much is gained by using cascade elements of enrichment factor less than 2. Since interstage coupling represents also a considerable cost and energy item, a balance has to be made between number of stages and total volume. It is likely that the choice will be for a stage gain of 4–6.

The strong dependence of the volume on $(\alpha - 1)$ is emphasized in Equation 11.

For actual design problems it is useful to tabulate the function U for various possible parameters. In Tables I and II are given minimal values of U (as

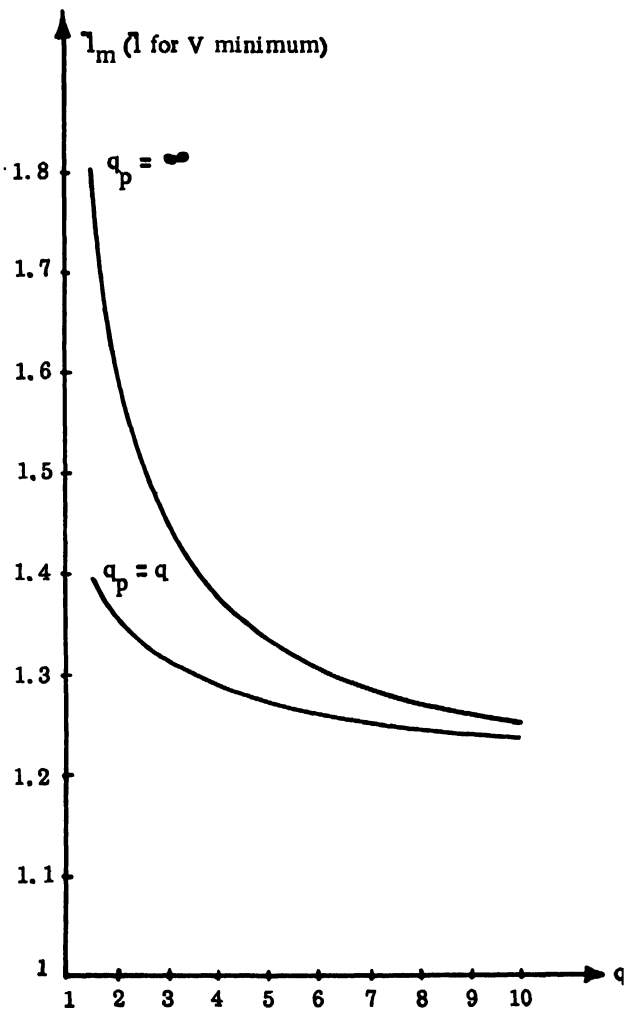

Figure 4

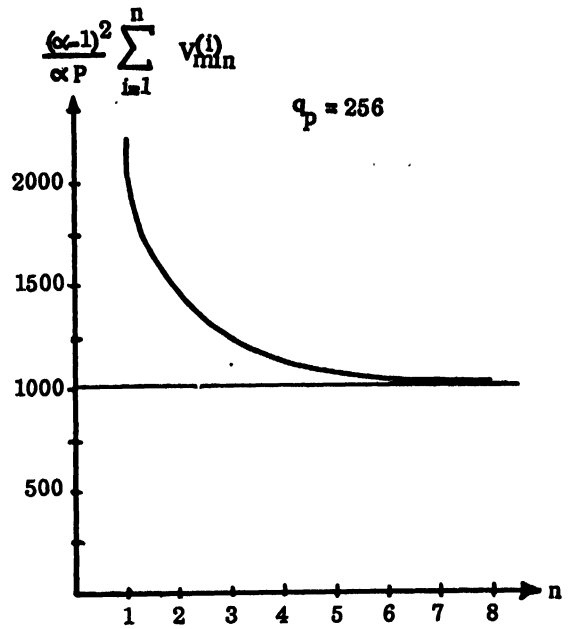

Figure 5

function of) and the corresponding values of Q, $(Q_\infty - 1)$, and $\Omega_0 \cdot Q_\infty$ is the enrichment which would be obtained under the same condition in an infinitely efficient column and is given by:[2]

$$Q_\infty = 1 + \frac{\alpha - 1}{\alpha} \times \frac{L}{P}$$

Ω_0 is the value which Ω takes with no production and is given by:

$$\Omega_0 = \frac{k(\alpha - 1)V}{L}$$

The way in which these tables have been constructed is described in the appendix. The upper entry in each space refers to $\alpha = 1.0$ and the lower refers to $\alpha = 1.05$. It is seen that for most values of variations in α may be neglected. This, of course, is the reason for the choice of these particular parameters in the design equations.

Table I

Ω	$Q_\infty - 1$	Q	U	$\bar{I}_{min}$	Ω_0
2	1.19	1.89	1.20	1.34	1.08
	1.28	1.94	1.49	1.36	1.16
2.5	2.47	2.89	4.37	1.30	1.77
	2.54	2.93	4.65	1.31	1.83
3	4.36	4.40	10.63	1.28	2.44
	4.51	4.50	11.11	1.29	2.46
3.5	7.17	6.71	22.02	1.26	3.07
	7.22	6.78	22.35	1.25	3.09
4	9.90	9.22	35.96	1.21	3.63
	9.96	9.27	36.38	1.21	3.65
5	27.48	24.03	132.6	1.19	4.82
	27.53	24.07	133.1	1.19	4.83
5.5	42.30	36.91	227.3	1.18	5.37
	42.35	36.95	227.8	1.18	5.37
6	65.06	56.89	384.4	1.16	5.90
	65.11	56.94	385	1.16	5.91
6.5	100.16	87.96	644.6	1.15	6.44
	100.21	88.08	645.03	1.15	6.44

If α, k are taken as fixed parameters there remain Q, V, L, P as variables. The requirement of minimal U limits the number of free variables to any two of the four listed above. There are, thus, six possible combinations or six types of problems which may be solved. Some examples illustrating the use of these tables are given below.

1. A plant is required to produce P moles per day at an enrichment Q, determine the minimum volume of the packing and the required flow. Using Table I we read against the given Q the values of U and $Q_\infty - 1$. From the value of U the volume V is calculated from the equation $V = \alpha PU/k(\alpha - 1)^2$. The flow L is calculated from the equation

$$L = \frac{\alpha(Q_\infty - 1)P}{\alpha - 1}$$

2. Given a certain available flow L, it is desired to determine that amount of product at enrichment Q, which will cost least. This problem may arise, for instance, if a given amount of waste heat has to be utilised in heavy water production. The requirement for least cost means a maximum production per unit volume of packing. This condition is easily found from Table I. Against the entry of Q in this table we read off values for $Q_\infty - 1$ and Ω_0. From these quantities the derived values of V and P are calculated using equations:

$$V = \Omega_0 L/k(\alpha - 1)$$
$$P = L(\alpha - 1)/\alpha(Q_\infty - 1).$$

3. It is desired to produce material at enrichment Q, given a certain column of volume V. It is required to determine the maximum production P, which is possible and the appropriate flow. Again we read off from Table I values of Ω_0 and U corresponding to the given Q, and calculate P and L from the equations:

$$P = k(\alpha - 1)^2 V/U$$
and
$$L = k(\alpha - 1)V/\Omega_0$$

4. Given a certain column of volume V producing a quantity P of enriched material, it is required to determine the maximum enrichment possible and the appropriate value of the flow L. We find U from the formula:

$$U = \frac{kV(\alpha - 1)^2}{P}$$

Using this value in Table I we read off directly Q. From the same table we also read off the value of Ω_0 from which we compute the required flow as in example 3. This problem has been solved without using the tables by Dostrovsky, Gillis and Vromen.[4]

The other possible problem, where L and P or L and V are given, cannot be solved without setting an additional economic value to the product PQ.

Table II

Ω	$\frac{\alpha-1}{\alpha}\times\frac{L}{W}$	Q	U	$\bar{l}_{min}$	Ω_0
—1	0.28	0.80	0.110	1.40	0.4
	0.37	0.72	0.194	1.32	0.5
—0.5	0.70	0.52	0.83	1.46	1.2
	0.72	0.49	0.75	1.41	1.0
—0.1	0.95	0.37	1.73	1.51	1.8
	0.95	0.36	1.72	1.48	1.8
0.5	1.21	0.21	3.45	1.53	2.9
	1.22	0.22	3.24	1.56	2.7
1	1.37	0.14	5.09	1.59	3.7
	1.38	0.14	4.84	1.60	3.5
2	1.57	0.054	8.66	1.66	5.5
	1.58	0.054	8.33	1.67	5.3
3	1.68	0.021	12.4	1.72	7.4
	1.70	0.021	12.0	1.73	7.1
4	1.75	0.008	16.3	1.76	9.3
	1.77	0.008	15.8	1.77	8.9
5	1.80	0.003	20.3	1.81	11.3
	1.82	0.003	19.7	1.82	10.8

The design of a column having both stripping and enriching sections can also be made readily using Tables I and II and Fig. 2. If the feed is liquid at the boiling point the flow of vapour in both sections is equal. The products at both end are given in terms of the feed F, by:

$$P=\frac{1-Q_w}{Q_p-Q_w}F$$

and

$$W=\frac{Q_p-1}{Q_p-Q_w}F$$

and

$$l_{min}=\frac{\alpha}{\alpha-1}\cdot\frac{(Q_p-1)(1-Q_w)}{Q_p-Q_w}F$$

If P, W, Q_p and Q_w are given, we can calculate the volumes and flows of each separately, using Tables I and II as was done in example 1. However, it will be found that, in general, the values of $\bar{l}$ for the two sections will not be identical. Since l_{min} is the same for the two sections, it follows that we cannot maintain the requirement of minimum volume in both at the same time. An actual solution can make use of a plot of U against $\bar{l}$ as in Fig. 2 to determine the best combination of $\bar{l}$ and the sum of the volumes.

Once the volume of the column has been fixed, it is possible to proceed with the determination of the height and diameter of the apparatus. Since $V=Z\times A$, when A is the cross sectional area of the column and Z its height, a considerable latitude in the proportionating of the column exists. The range of variation of A is limited on the lower side by the maximum permissible flow density Λ. This is a characteristic of the packing material used. In any design we may choose any flow density, up to the maximum possible, and this choice will determine A, since $A=L/\Lambda$ and hence Z. The use of the maximum flow density will give columns of maximum height and smallest diameter. Any lower value of Λ will give lower and wider columns.

This argument is strictly valid, of course, only for ideal packing materials were k is independent of Z, A and α. Since for many materials this is not the case, the range of choice is more limited and considerable thought has to be given to the appropriate dimensioning of the plant.

APPENDIX

Another form of Equation 11 is:

$$Q=\frac{Q_x}{1+(Q_\infty-1)}$$

where $$\Omega=UQ_x/(Q-1)(\alpha Q_\infty-1)$$

$$U=\frac{kV(\alpha-1)^2}{\alpha L^2}$$

and[2,4] $$Q_x=1+\frac{\alpha-1}{\alpha}\times\frac{L}{L'}$$

The requirement for maximum Q as a function of Q_x-1 when U is kept constant leads to the condition that:

$$(Q_x-1)^2-2(Q_x-1)x-\frac{\alpha-1}{\alpha}(2x+1)=0$$

where

$$x=[e^{\Omega}-1)/2]-1$$

Tables I and II were constructed by taking values for Ω and calculating x and then, from the quadratic equation, (Q_x-1). These values were entered in the second column of the tables. (For the case of $Q<1$, $\frac{\alpha-1}{\alpha}\times\frac{L}{W}$ was entered). The value of Q, U were then calculated from $(Q_\infty-1)$ and Ω, and entered in the third column and fourth columns. l_{min} was computed from the equation:

$$\bar{l}_{min}=(Q_x-1)/(Q-1)$$

and entered in the fifth column.

Finally Ω_0 was computed from values of $U/(Q_x-1)$ and entered in the sixth column.

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Final Concentration of Heavy Water by Rectification

By P. Baertschi and W. Kuhn,* Switzerland

During the past years we have developed rectifying columns by which solutions of heavy water with any D_2O content can be concentrated to pure D_2O in continuous operation and on a technical scale. This process is, for various economical reasons, advantageous as soon as the initial D_2O concentration exceeds some tenths of a per cent, and it becomes very efficient for final concentration up from about 1%.

The flow of water (liter) and the energy (kwh) which are necessary to produce 1 kg of pure D_2O in any kind of rectifying column if no steam recompression is applied are given in Fig. 1 as functions of the initial D_2O concentration for distillation temperatures of 50° and 100°C respectively (curves I). The required number of theoretical plates (for total reflux) in order to reach a final concentration of 99.8% D_2O is represented for 50°C and 100°C respectively by the curves II.

According to Fig. 1 it is in principle favourable to distill at low temperature and pressure in order to diminish the column size and the consumption of energy. On the other hand, steam recompression is more favourable at high pressures, and therefore an intermediate distillation pressure should be chosen in this case. By the use of steam recompression the energy consumption can be diminished to a small fraction of the figures given by curve I in Fig. 1, provided that the pressure drop in the rectifying column is low.

DEVELOPMENT OF HIGHLY EFFICIENT RECTIFYING COLUMNS

The development of certain type of rectifying columns featuring very high separation efficiency (low HETP) was started by Kuhn[1] in 1940. The basic principle of the Kuhn column consists in a multiplicity of narrow, parallel-working fractionating tubes with individual reflux and including means by which the desired reflux ratio can be maintained constant and equal over all the tubes. Thus, the separation efficiency of the whole column is exactly as high as that of a single fractionating tube, whereas the production capacity is proportional to the number of tubes in the column. This principle therefore allows the reliable design and construction of large columns with high separating power on the basis of the performance data of one single tube.

Since 1945 we have been studying the possibilities of applying the Kuhn column to the separation of the water isotopes.

The preliminary experiments with narrow empty tubes (corresponding to the original type of the Kuhn column) have not been very successful because the low HETP calculated from the theory of Kuhn[1] could not be reached by far in the case of water. This discrepancy was most probably caused by the bad wetting power of water which prevented the formation of a uniform, thin film in the tubes. Although D_2O enrichment factors of 20 per meter and very low pressure drops could be achieved, the empty-tube column was considered to be much too expensive and too delicate for any large scale enrichment of D_2O. It should, however, be emphasized that the empty-tube column yielded the theoretically expected very high separating power in the case of organic mixtures.

Much more promising results were obtained with packed fractionating tubes. It is a well known fact that packed fractionating tubes lose separating power with increasing diameter due to the increasing probability of non-uniform liquid and vapour distribution. This loss of separating power can, of course, be completely avoided by applying the principle of the Kuhn column.

For a proper specific throughput of some 100 ml per hour per cm^2, the best separating efficiency of about 50–60 theoretical plates per meter was obtained in tubes of a few cm diameter and with highly wettable packings, like wire-gauze rings and different types of helices. Our results on single packed tubes were quite similar to those obtained independently by Dostrovsky *et al.*[2]

In order to investigate the possibility of continuous final concentration of D_2O on an industrial scale by means of packed-tube Kuhn columns, a two-stage pilot plant was built, designed to concentrate D_2O from 0.1–1% to 99.8% with a yield of at least 90%. The design was based upon the experimental results obtained for HETP and throughput in a single fractionating tube. The lengths of the rectifying and the stripping sections, as well as the proper reflux ratios at the lower and upper end of the column respectively were calculated by using the relations derived by Kuhn.[3]

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The pilot plant project was fully supported by the Swiss Atomic Energy Commission (SKA).

DESCRIPTION OF THE PILOT PLANT

The first stage of the pilot plant is shown schematically in Fig. 2.

The Kuhn column consists of a rectifying and a stripping section. The feed water to be concen-

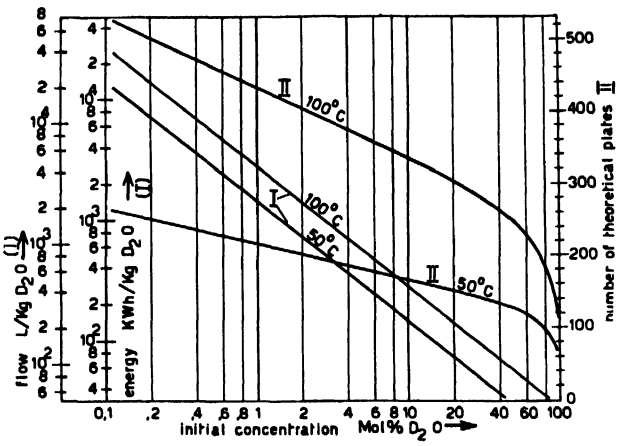

Figure 1. Flow and energy required for the final concentration of D_2O: Curve I, flow (throughput) through column (liter) and energy (kwh) required to produce 1 kg of pure D_2O without steam recompression; Curve II, required number of theoretical plates to reach a final concentration of 99.8% D_2O, (total reflux)

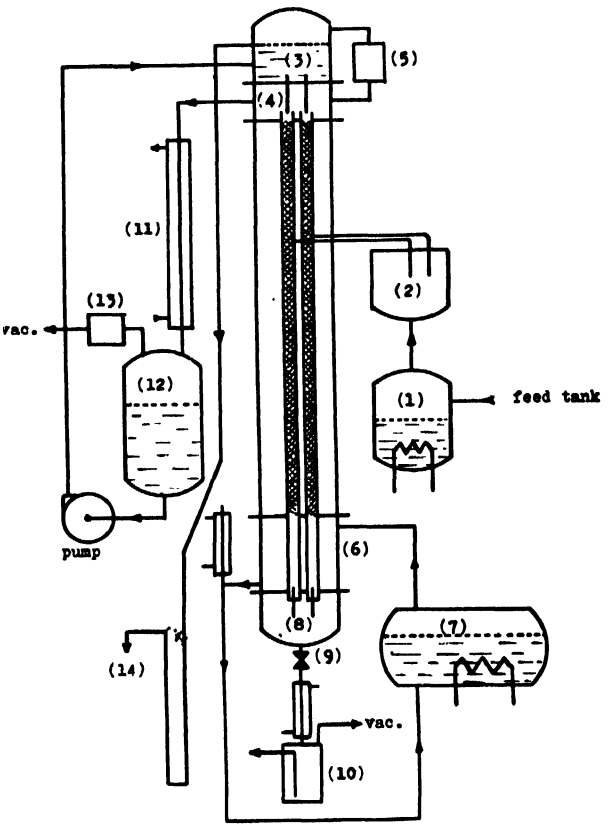

Figure 2. Pilot plant for the final concentration of D_2O, I. stage

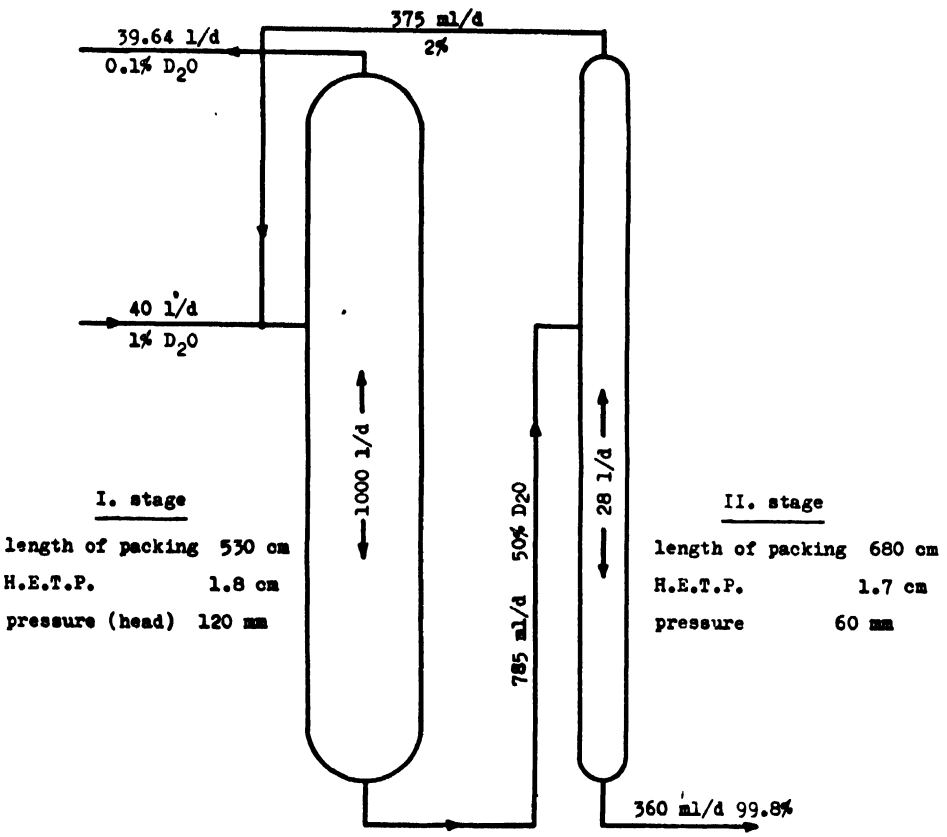

Figure 3. Flow diagram and data of the pilot plant

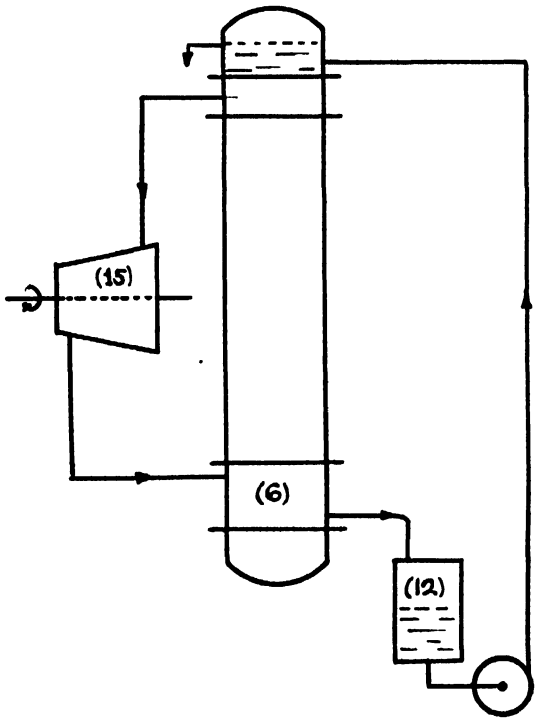

Figure 4. Water rectification using steam recompression

trated is continuously evaporated in the boiler (1), and the steam is equally distributed by means of superheated capillaries in (2) to the various fractioning tubes. The overhead water in (3) is equally distributed by capillaries as reflux to the fractioning tubes, the flow beeing controlled by the pressure difference between (3) and (4) maintained by a differential manostat (5). The lower part of the fractionating tubes is superheated by steam entering into the heating chamber (6) from the steam generator (7). Since the distillation is carried out under reduced pressure, maintained by the manostat (13), all the downflowing water is completely evaporated along the inner walls of the fractionating tubes in the region of (6) whilst the corresponding amount of heating steam is condensed at the outer surface of the tubes. The lower ends of the tubes are almost closed by superheated capillaries through which the proper small amount of the enriched D_2O steam is withdrawn into the common chamber (8), through the flow control valve (9) and finally, after condensation, into the storage flask (10). The steam ascending in the fractionating tubes leaves the upper open ends in (4) and is condensed completely in (11). The stripped condensate in (12) is pumped back into the container (3) from where a certain amount of feed, is leaving the column by a barometric overflow (14).

The second stage, whose feed boiler is fed by the D_2O concentrate in (10) is working almost exactly in the same way as described for the first stage.

Some data of construction and performance of the complete pilot plant are given in the flow diagram Fig. 3.

The pilot plant was tested and improved during some 20 months of operation. The separating power was found to remain constant and steady conditions could easily be maintained. According to our most recent improvements the rectification can be performed completely automatically and need thus only very little supervision. The time to reach equilibrium is rather short according to the low holdup and was found to be about 10 days for the first stage and about 2 days for the second stage.

KUHN COLUMNS FOR LARGE SCALE FINAL CONCENTRATION OF D_2O

The favourable results obtained with the pilot plant suggest the application of the Kuhn column to the large-scale final concentration of heavy water.†

If the initial concentration of D_2O is low, the energy consumption for the final concentration will be correspondingly high, according to Fig. 1. In order to lower the energy input to large-scale Kuhn columns, steam recompression might be applied. In this case, which is schematically represented by Fig. 4, the steam leaving the column head is condensed as heating steam in the heating chamber (6) after having been brought to a sufficient high saturation pressure and temperature by means of the compressor (15). The water condensed in (6) is pumped back from the container (12) to the head of the column.

It should be noted, that the compressor needs only as much energy as is required to overcome the resistances in the transfer of heat and material in the column. These resistances are rather low in the Kuhn column, due to the low pressure drop of only about 0.3 mm Hg per plate and to the good heat transfer through the fractionating tubes in the heating chamber. Consequently, the application of steam recompression is very favourable for large-scale Kuhn columns and diminishes the energy consumption given by Fig. 1 by a factor between 5 and 10 for normal vacuum operation.

ACKNOWLEDGEMENTS

We wish to thank Dr. P. Massini for carrying out many of the preliminary studies and Mr. M. Thürkauf for his efficient help in the construction of the pilot plant.

The preliminary studies have been supported mainly by the BIGA, Berne, the work connected with the design and construction of the pilot plant was supported by the Swiss Atomic Energy Commission.

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† Large-scale Kuhn columns with or without steam recompression are being designed and constructed by Sulzer Bros. Ltd., Winterthur.

Efficiency of Some Catalysts in the Exchange Reaction Between Heavy Water and Hydrogen

By Pavle Savić, Slobodan Ribnikar and Bošco Pavlović, Yugoslavia

The isotopic exchange between hydrogen and water was first observed by Horiuti and Polanyi[1] and Bonhoeffer and Rummel,[2] while the theoretical interpretation was given by Libby[3] and Kimball and Stockmayer.[4]

The exchange reaction requires the aid of catalysts in order to be effected with a measurable velocity. There exist many papers treating the subject of the exchange between hydrogen and water on metal surfaces.

In the group of oxide and mixed catalysts a quick exchange between deuterium and water retained on catalytic materials: (chromium trioxide, zinc oxide, zinc chromate and alumina) was observed at higher temperatures.[5] Savić, Ribnikar and Dogramadži[6] found that the exchange between water, steam and hydrogen on surfaces of nickel tungstate at 11°C was respectively 25, 40 and 82 times greater than the rate of the exchange on zinc chromate, manganese chromate and chromium trioxide respectively.

Assuming the possibility of a similar behaviour of compounds which are analogous to nickel tungstate we have examined the properties and the catalytic activity of reduced tungstates, chromates and molybdates of nickel, cobalt and iron, of tungstates and molybdates of chromium, and for comparison purposes we have examined by an analogous process the behaviour of reduced oxides of nickel and cobalt and of a platinum catalyst.

PREPARATIVE PART

Preparation of Tungstates

The first three tungstates were obtained by the method used for the nickel tungstate by Rohrer, Rooley and Brown,[8] i.e., by precipitation from aqueous solutions. The starting substances were $Na_2WO_4 \cdot 2H_2O$ C.P. (Mallinckrodt), $NiCl_2 \cdot 6H_2O$ C.P. (Mallinckrodt), $Co(NO_3)_2 \cdot 6H_2O$ P.A. (Merck) and $FeCl_3 \cdot 6H_2O$ P.A. (Merck). The solutions were mixed in equivalent quantities. The salts of nickel and cobalt were precipitated from hot solutions, while the iron salt was precipitated in the cold state. The precipitates obtained $NiWO_4 \cdot 6H_2O$, $CoWO_4 \cdot 2H_2O$, and $Fe_2O_3 \cdot WO_3 \cdot 4H_2O$ were washed with water till the disappearance of chloride or nitrate ions respectively. The precipitates were dried at a temperature of 110°C.

Chromium tungstate was obtained by mixing a solution of $CrCl_3 \cdot 6H_2O$ P.A. (Merck) with a solution of sodium tungstate in equivalent proportions. The bluish-green precipitate turned a dark green colour, after the washing and drying process.

Preparation of Chromates[7]

By mixing hot solutions of equivalent quantities of $NiCl_2 \cdot 6H_2O$ C. P. (Mallinckrodt) and $(NH_4)_2CrO_4$ C.P. (Mallinckrodt) a crystalline reddish-brown precipitate of $Ni(NH_4)_2CrO_4 \cdot 6H_2O$ was obtained. This precipitate was washed with a dilute solution of ammonium chromate and dried at a temperature of 110°C.

A cobalt ammonium chromate precipitate was obtained in an analogous way starting from $Co(NO_3)_2$ P.A. (Merck) and $(NH_4)_2CrO_4$ C.P. (Mallinckrodt). The colour of the precipitate was bluish-black.

By mixing equivalent quantities of a solution of $FeSO_4 \cdot 7H_2O$ P.A. (Merck) and a solution of $(NH_4)_2CrO_4$ C.P. (Mallinckrodt) in the cold state a gelatinous precipitate of a yellowish-brown colour was immediately obtained. The precipitate was washed and dried at 110°C.

Preparation of Molybdates

The molybdates were obtained starting from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ P.A. (Merck) and $NiCl_2 \cdot 6H_2O$ C.P. (Mallinckrodt), $Co(NO_3)_2 \cdot 6H_2O$ P.A. (Merck), $FeCl_3 \cdot 6H_2O$ P.A. (Merck) and $CrCl_3 \cdot 6H_2O$ P.A. (Kahlbaum). The salts of nickel, iron and chromium are precipitated in cold state while for the cobalt salt heating is required. The precipitates were washed with a solution of ammonium molybdate and dried at 110°C. The precipitate of the nickel salt is bright-blue, the cobalt salt is violet blue and the moist iron salt is bright green, but yellow when dried. The chromium salt is rose-coloured in the wet state, but violet when dried. All precipitates are crystalline.

Other Catalysts

From a solution of $NiCl_2$ C.P. (Mallinckrodt) sodium hydroxide precipitates nickel hydroxide. The solution was washed by decantation till the disappearance of Cl-ion both in the solution and the precipitate.

A precipitate of $Co(OH)_2$ was obtained by the action of sodium hydroxide on a solution of cobaltous nitrate. The precipitate of cobaltous hydroxide which was originally rose-coloured became the black cobaltic hydroxide during the washing process. It was washed till the disappearance of NO_3-ion and dried at 110°C.

A platinum catalyst was obtained in the following way: previously purified granulated activated charcoal (boiled with diluted hydrochloric and nitric acids) was soaked with a solution of chloroplatinic acid, then dried and subjected to reduction in a hydrogen stream at 180°C for 6 to 7 hours. Then it was boiled with water and dried in a vacuum. A sample, when analysed by usual methods, showed 2.54% Pt.

The substances to be used for the catalysis were partially crushed and screened through sieves taking fractions of 0.6 to 0.3 mm, with the exception of cobaltous ammonium chromate which was already a fine powder.

EXPERIMENTAL PART

Adsorption Properties of Catalysts

The various compounds, prepared in the way described above were reduced with hydrogen at 400°C with the exception of the platinized charcoal which was reduced at 180°C.

After 4 to 6 hours of desorption in vacuo at 180 to 200°C, the catalysts were prepared for adsorption measurements of the amount of the gas adsorbed catalyst adsorbs during 4 hours at 110°C (temperature of the exchange process) was determined. The measurements of the amount of the gas adsorbed was effected with an apparatus similar to that described by Harkins and Jura.[9] The reading of the pressures was effected with an accuracy of 0.01 mm Hg, and the dead space was determined by helium. The results are shown in Table I.

The determination of the surface areas of the catalysts was effected with pure nitrogen at the temperature of liquid nitrogen by the Huttig[10] and BET[11] methods which gave results in satisfactory agreement with each other. From the relation $r = 2V/A$ given by Emmett and De Witt,[12] where V represents the volume of pores in cm^3, A the surface area in cm^2/gm, the mean radius vs the volume of the pores was determined.

Exchange Apparatus

The apparatus is schematically shown in Fig. 1. The hydrogen obtained from pure zinc and hydrochloric acid and purified by usual methods, enters the moistening tube A which is placed in water kept at a constant temperature. The wet hydrogen passes through a heated connection tube into the catalytic tube B which is submerged in an oil bath. The catalyst is placed at the point marked K. After the reaction, the water is frozen out in the liquid air trap C and the hydrogen then enters a device for the measurement of the gas volume.

The reduction and activation of catalysts was effected *in situ* with pure hydrogen at 400°C for a period of 3 hours with a hydrogen flow of about 5 litres per hour.

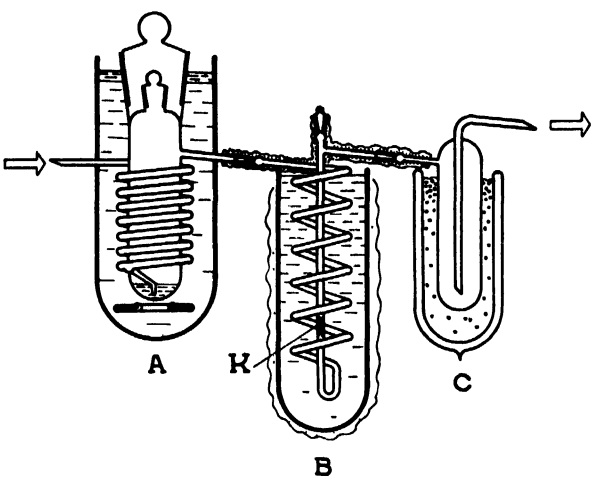

Figure 1

Table I

Catalyst	Surface area S in m^2/gm	Amount H_2 adsorbed at 110°C in cm^3 per gm	Mean pore volume in mm^3	Effective density in gm/cm^3	Rate constant k in sec^{-1}	Half-time of exchange in sec	Equal area activity $A = 10^3 k/S$
Ni-W	26.2	0.50	0.033	7.0	2.22	0.31	85
Cr-W	29.8	0.08	0.026	9.0	1.19	0.58	40
Co-W	37.0	0.21	0.040	12.5	0.32	2.17	9
Fe-W	21.7	0.03	0.023	8.2	0.00	–	0
Ni-Cr	256.8	3.90	0.352	1.5	4.65	0.15	18
Co-Cr	201.3	3.25	0.261	2.0	0.60	1.15	3
Fe-Cr	113.0	1.69	0.140	4.9	0.00	–	0
Ni-Mo	147.7	7.45	0.149	2.7	2.26	0.31	15
Cr-Mo	195.0	1.90	0.203	4.2	0.21	3.38	1
Co-Mo	96.6	3.75	0.119	2.4	0.15	4.50	1.6
Fe-Mo	49.5	0.20	0.046	4.5	0.00	–	0
NiO	45.2	10.62	0.052	6.0	0.39	1.76	9
CoO	50.3	3.40	0.056	3.7	0.00	–	0
Pt*	580.0	0.70	0.476	2.5	0.88	0.79	–

* Platinum on activated charcoal with 2.54% Pt. The surface area is measured for both platinum and charcoal.

The moistening tube was kept at a constant temperature of $66 \pm 0.5°C$ and the catalytic tube at $110 \pm 1°C$ in all experiments. The catalytic tube, having a diameter of 5.1 mm, was filled with substances to be investigated at heights from 0.5 to 3.0 cm, according to the requirements of each case. A small quantity of glass wool was placed below and above the contacts since small particles of the catalyst may escape with the gas during the reduction process.

The mole ratio H_2/H_2O varied in the experiments from 3.9 to 4.2 depending on the velocity of the hydrogen flow which varied from 1.2 to 1.6 litres per hour, and in exceptional cases was higher or lower than that.

The moistening tube in all experiments was filled with 1.00 ml of water containing 0.524% D_2O.

The concentrations of heavy water were measured on a mass spectrometer with an error of $\pm$ 0.006%.

Calculation of Results

The decrease of the concentration of HDO in the original sample was taken as a measure of the catalytic activity.

In order to define exactly the contact time of the gas with the catalyst it was necessary to find its effective volume. The volume of each reduced substance was found by use of helium. The mass divided by this value gives the number which indicates the specific weight, σ, of this body together with the closed isolated cavities into which the gas can not enter (Table I indicates the values for each substance). The volume of the contact space v_0 has been calculated according to the equation

$$v_0 = v - M/\sigma$$

where v represents the directly measured total volume of the catalytic space.

The contact time, t, was calculated from the flow velocity taking into account the calculated contact space.

The rate constant of the reaction was calculated according to the equation

$$k = \frac{1}{t} \ln \frac{C_0 - C_\infty}{C_t - C_\infty} \cdot \text{sec}^{-1}$$

where C_0 represents the starting concentration of D_2O, C_t the measured concentration after the exchange and C_∞ the calculated concentration for the equilibrium state in the conditions of the experiment.

The equal area activity of the catalysts, A, was calculated according to the equation

$$A = 10^8 k/S$$

where S represents the surface area of the catalyst in m^2 per gram of substance.

Example of Calculations of Results

Catalyst Ni-Cr; weight 0.080 gm; volume 0.319 cm^3; water quantity 1.00 ml; hydrogen quantity 5340 cm^3; duration 14,100 sec. From the weight, volume and effective density the volume of the catalyst spaces is found:

$$v_0 = v - (M/\sigma) = 0.319 - (0.080/1.5) - 0.267 \text{ cm}^3$$

The hydrogen at 110°C has a volume of 6979 cm^3 and one gram of water gives 1744 cm^3 of steam, which makes a total of 8723 cm^3.

The gas stays in the catalytic space for a time of $(14{,}100 \times 0.267)/8723 = 0.446$ sec, which is the value of the contact time t.

Taking for the equilibrium constant K of the reaction at 110°C the value

$$K = \frac{[H_2]\,[HDO]}{[HD]\,[H_2O]} = 2.54$$

The constant has been theoretically calculated by Libby[3] and agrees well with the measurements. According to the above conditions, the starting concentration of 0.524% D_2O should fall to 0.299%.

A value of 0.265% has been found. The rate constant of the reaction is equal to

$$k = \frac{1}{t} \ln \frac{C_0 - C_\infty}{C_t - C_\infty} = \frac{2.3}{0.446} \times \log \frac{0.524 - 0.229}{0.265 - 0.229} = 4.71 \text{ sec}^{-1}$$

From this follows that the value of the half-time of the exchange is equal to

$$T_{1/2} = 0.693/4.71 = 0.15 \text{ sec.}$$

CONCLUSION

From the experimental data it can be seen that the equal area activity decreases rapidly in the series Ni > Cr > Co > Fe and an equally clear decrease is found in the series $WO_4 > CrO_4 > MoO_4$, with a small exception in the case of Co–Cr (see Table II).

Table II.

	Tungstates	*Chromates*	*Molybdates*	*Red. Oxides*
Nn	85	18	15	9
Cr	40	—	1	0.4*
Co	9	3	1.6	0
Fe	0	0	0	0*

* Values for the activity of oxides of chromium and iron are calculated from Ref. 6.

ACKNOWLEDGEMENT

The authors are grateful to Miss N. Dogramadzi for the measurements of heavy water concentrations.

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Modification in the Electrolytic and Exchange-Reaction Process for the Production of Heavy Water

By J. L. Otero and M. Gispert,* Spain

The present paper presents a study of the production of heavy water[1] using a cascade of electrolysis cells giving hydrogen, and a cascade of reactors in which the isotopic exchange reaction is carried out in order to recover the deuterium from the hydrogen; using, in all of them, ordinary steam with a heavy-water concentration equal to that of natural water, and having, in each group of cells, one, two or more reactors, for intermediate condensation of the enriched steam.

The flow diagrams, Figs. 1 and 2, show an installation of this type. It will be seen very clearly from those diagrams how the cascades are arranged, so that we leave out their description.

Before we show how to make the computations pertaining to an installation of this type, it is necessary that we clarify the concepts to be used for a better understanding of what is involved.

If we call X the molar fraction of HDO in steam and Y the molar fraction of HD in the hydrogen, the separation factor S, between the electrodes of a cell is

$$S = \frac{\dfrac{[HDO]}{[H_2O]}}{\dfrac{[HD]}{[H_2]}}$$

It can be written in the following fashion:

$$S = \frac{\dfrac{X}{1-X}}{\dfrac{Y}{1-Y}} \qquad (1)$$

By analogy, for HDO concentrations lower than 0.04, in the isotopic exchange reaction:

$$H_2O + HD \leftrightarrows HDO + H_2$$

The equilibrium constant:

$$K = \frac{[HDO]\,[H_2]}{[H_2O]\,[HD]} = \frac{\dfrac{[HDO]}{[H_2O]}}{\dfrac{[HD]}{[H_2]}}$$

This can be written as follows, with an asterisk to make a distinction between the variables:

$$K = \frac{\dfrac{X^*}{1-X^*}}{\dfrac{Y^*}{1-Y^*}} \qquad (2)$$

Both Equations 1 and 2 can be simplified as follows:

$$S = \frac{X}{Y} \qquad (3)$$

and

$$K = \frac{X^*}{Y^*} \qquad (4)$$

with a negligible error at D_2O concentrations in water lower than 2%.

By a graphical representation of Equations 3 and 4 (Fig. 3), we obtain two straight lines which pass through the origin of the coordinates, with slopes of $1/S$ and $1/K$ respectively. The points on the straight line of $1/S$ slope indicate the concentrations of X and Y which correspond to heavy water in the electrolyte and deuterium in the hydrogen which releases it. Those corresponding to the straight line of $1/K$ slope represent the concentrations of X^* and Y^* which leaves an ideal catalytic zone where the conversion rate was 100%.

The enrichment of heavy water by the electrolytic phenomenon and the isotopic exchange-reaction were conjugated in this graph in the following manner:

Let X_n be the D_2O concentration of the electrolyte of a cell group n; the hydrogen which comes from this cell will have a deuterium concentration represented by Y_n (point A). In order to recover the deuterium, the hydrogen is mixed with water vapour with a D_2O content equal to that of natural water, namely 0.015% molar. For the point which represents the mixture, we shall find point B ($X_{mat} = 0.015$; Y_n). When this mass of steam and hydrogen reaches a catalytic zone, we find that the concentrations of D_2O and D_2 in the water vapour and hydrogen respectively vary, and that the water vapour becomes richer, while the hydrogen becomes poorer. In order to determine the composition at the outlet of the reactor, if we let A be the molar steam concentration, and E the molar concentration of hydrogen which flows

Original language: Spanish.
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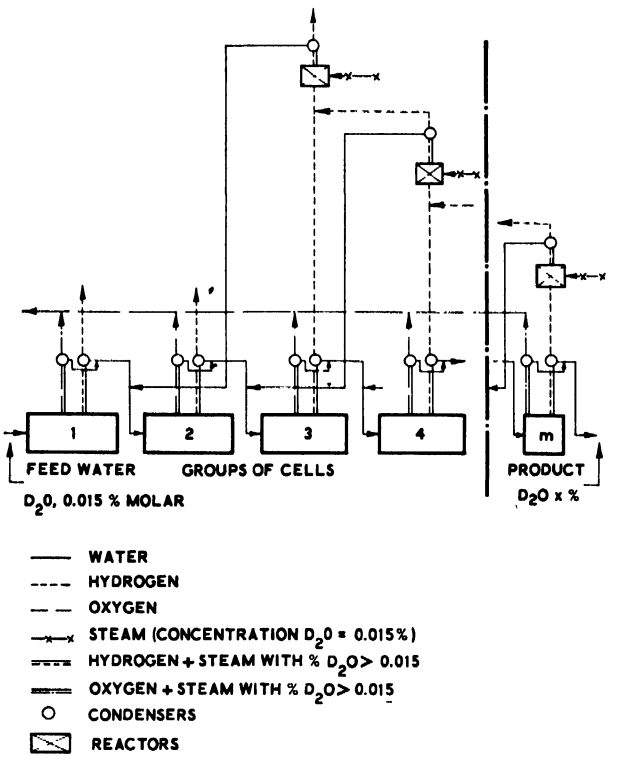

Figure 1

through the zone per time unit, the following equation must be satisfied:

$$AX_{nat} \times EY_n = AX_n^* \times EY_n^* \qquad (5)$$

in which X_n^* and Y_n^* are the D_2O and D_2 compositions of the steam and hydrogen respectively, after the mixture goes through the catalytic zone, in which equilibrium has been reached. Equation 5 can be written as follows:

$$\frac{A}{E} = \frac{Y_n - Y_n^*}{X_{nat} - X_n^*} = \alpha_n \qquad (6)$$

in which α_n is the ratio moles of water/moles of hydrogen in the mixture which reaches the reactor, corresponding to cell group n. If we allow for the fact that point C, the coordinates of which are (X_n^*, Y_n^*) must be on the line which represents the equilibrium of the exchange reaction on the graph, we shall find it readily by simply drawing, through point B (X_{nat}, Y_n), a straight line of slope A/E, and the point of intersection on the line of equilibrium will set the composition sought. We would obtain the same results analytically by solving (4) with (6), which gives steam having a D_2O concentration greater than that of natural water, at the expense of the D_2 present from the hydrogen which has been depleted in the isotope concentration installation and the flow diagram shown. We shall then have the following ratios:

$$\begin{aligned} Y_n^* &= Y_{n-1} \\ X_n^* &= X_{n-2} \end{aligned} \qquad (7)$$

and it will be possible to repeat the balance sheet shown in the reactor, of group n, for $n - 1$.

Graphically, the values (X_{n-1}, Y_n), (X^*_{n-1}, Y^*_{n-1}), (X_{n-2}, Y_{n-2}) ... can be fixed, from the earlier relationships of Equation 7. We shall see from Fig. 4 that they define, between the equilibrium lines $1/K$ and $1/S$, a series of steps which terminate in that corresponding to Y_3^* which is equal to Y_2.

On finding the latter, we shall readily see from the graph that once we assign certain fixed values to K and S, the compositions in all groups of cells and reactors will be defined.

Analytically, we reached the values of these concentrations merely by fixing Y_2, computing X_2 by the $X_2 = S \times Y_2$ ratio, and from those, all the other values allowing for the fact that the following formula must be satisfied:

$$\begin{aligned} X_n &= \frac{S}{K} X_{n-1} \\ Y_n &= \frac{S}{K} Y_{n-1} \end{aligned} \qquad (8)$$

As regards the quantities of water which come out of each (P_n) group, and are electrolyzed (E_n), when we set one of them in a group, the others remain fixed in addition to Y_2. In effect, if we represent the last group by subindex m, we can write:

$$P_{m-1} = P_m + E_m$$
$$P_{m-1}X_{m-1} = P_mX_m + E_mY_m$$

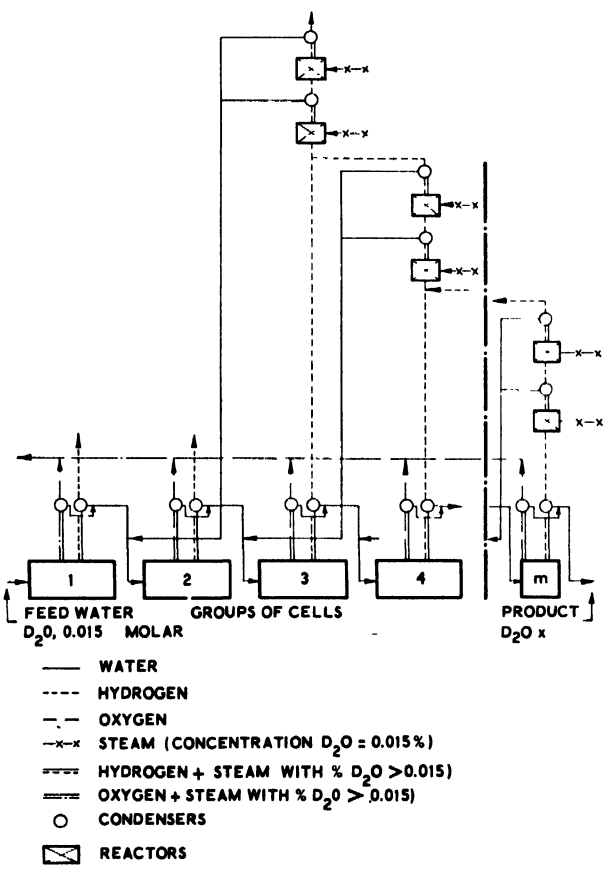

Figure 2

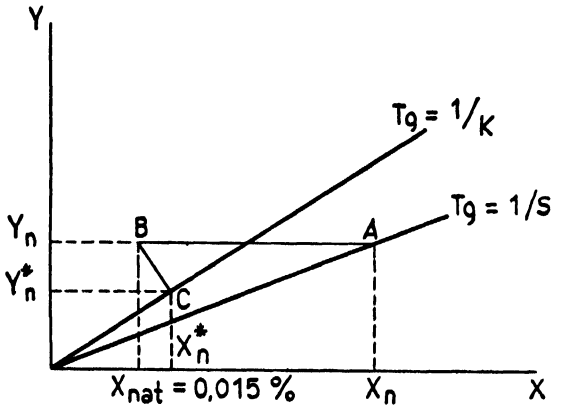

Figure 3

which readily gives:

$$P_m(X_m - X_{m-1}) = E_m(X_{m-1} - Y_m)$$

If we write $P_m = 1$ and allow for Equations 5 and 8 we obtain:

$$E_m = \frac{X_m - X_{m-1}}{X_{m-1} - Y_m} = \frac{S - K}{K - 1} = R$$

If we continue drawing up the equilibria of materials for the other groups, we readily get:

$$E_n = RP_n$$

$$E_n = \left\{ 1 + \sum_{i=n+1}^{m} E_i - \sum_{i=n+2}^{m} \left[\alpha_i \sum_{j=i}^{m} E_j \right] \right\} E_m$$

in which α_i is computed by means of Equation 6. For group 1

$$E_1 = P_1 \frac{X_1 - X_{nat}}{X_{nat} - Y_1}$$

and the corresponding feed:

$$P_0 = E_1 + P_1$$

For greater facility, the computations were done in the following manner: (1) determination of the concentrations after assigning values to K and S and giving a value to Y_2; (2) finding the values of

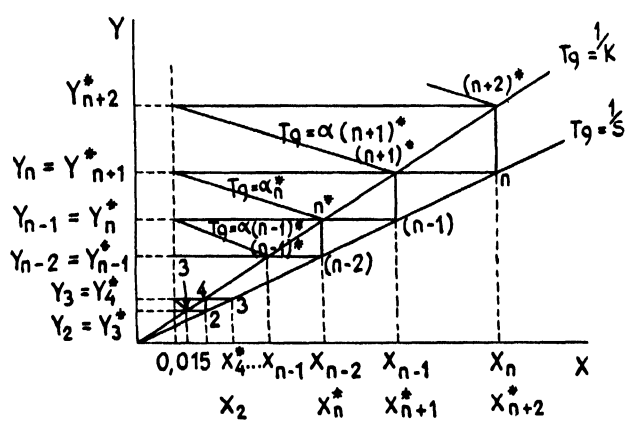

Figure 4

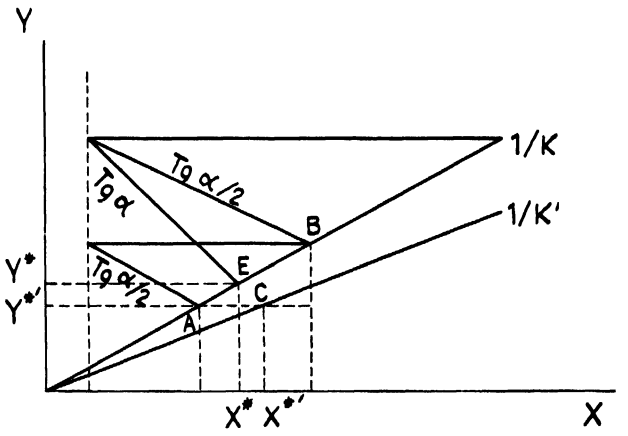

Figure 5

α_3, α_4, α_5; (3) set $P_m = 1$ and compute E_m; (4) find E_{m-1} and, from this, the value of P_{m-1} and then follow until the first group to which the last balances must be applied.

The efficiency of the setup is computed, allowing for:

$$\eta = \text{efficiency} = \frac{P_m X_m}{(\Sigma\alpha\Sigma E + P_0)X_{nat}} \times 100$$

The steam consumption and power of the installation for a given production of heavy water can readily be computed from $\Sigma\alpha\Sigma E$ and ΣE, allowing for the fact that these values refer to the quantity of heavy water produced.

If in a given group of cells, two catalytic zones are used instead of one, with intermediate condensation, and if we use, in each of them, equal quantities of steam in such a way that the sum be equal to that of the steam used in the case of a single catalytic zone, then if we follow in Fig. 5, the evolution of the system, we find that by uniting the water condensed in the two catalytic zones (points A and B), we obtain a mean heavy-water concentration (point C) greater than that obtained with a single zone (point E), and a value of Y, for the hydrogen which leaves the second zone, which also is lower. Accordingly, the system appears to function with an equilibrium constant $K' = X^{*\prime}/Y^{*\prime}$ greater than the real one $K = X^*/Y^*$.

If, as stated before, we establish that the quantity of steam used in each catalytic zone is the same, we can write the following equations:

For K':

$$EY_n + \alpha_n E X_{nat} = EY_n^{*\prime} + \alpha_n E K' Y_n^{*\prime}$$

and for K:

1st zone:

$$EY_n + \frac{\alpha_n E}{2} X_{nat} = EY^* + \frac{\alpha_n E Y}{2} K$$

2nd zone:

$$EY^* + \frac{\alpha_n E}{2} X_{nat} = EY^{*\prime} + \frac{\alpha_n E}{2} K Y_n^{*\prime}$$

from which we derive:

$$Y^* = \frac{Y_n + \frac{\alpha_n}{2} X_{nat}}{1 + \frac{\alpha_n}{2} K}.$$

an expression which gives us an equation:

$$(\alpha Y_n^{*\prime}) \times K^2 + [2(Y_n + Y_n^{*\prime}) - \alpha_n \ (2X_n^{*\prime} - X_{nat})] \times K - 4X_n^{*\prime} = 0$$

which gives, after the computation has been carried out in the form indicated above with the constant K' greater than that of equilibrium constant, the values of K which correspond to the two reactors. These values, divided by that of the equilibrium constant at the working temperature of the relevant catalytic zone, will give us the degree of conversion with which each one of them will operate.

By a similar line of reasoning, we reach, for the case of three catalytic zones, the following:

$$\alpha_n^2 Y_n^* K^3 + (9\alpha_n Y_n^* - \alpha_n^2 X_{nat})K^2 + [9Y_n + Y_n^*(18 - 9\alpha_n K')]K - 27K'Y_n^{*\prime} = 0$$

which enables us to make the same check-up as in the case before.

The graphs on Figs. 6 and 7 give an idea of the order of magnitude of the water consumption and of the efficiency of the installation as a function of Y_2. In them, we took for S, a value equal to 6; the installation for which we made the computation had 6 groups of cells and K' was assigned values of 3.1, 3 and 2.5, which represent three, two and one catalytic zone respectively, per group. The value of K is 2.5 in all the reactors.

As Y_2 goes down, the power of the first group also goes down and cancels out for the lowest value in each one of the curves shown. To this value, corresponds an installation with an exchange reaction starting from the second group.

In Fig. 8, we show the efficiency as a function of the number of groups for $K = 2.5$.

If we take the shape of these curves into account, as well as the P_n/E_n ratio in each group, and the temperature at which the cells work, it will be seen that it is possible to have a steam consumption of between 2.5 and 5.6 kg steam/gm D_2O, reaching concentrations of the order 1 to 2% with efficiencies of 35 to 45%. The values of K' oscillate between 2.5 and 3, which corresponds to an assumption of 2 or 2.5 for K, using two or three reactors with intermediate condensation in each group. As the concentration increases, the yield decreases, the installation is complicated and it is not of interest, therefore, to exceed a concentration of 1 to 2% of D_2O in the electrolyte of the last group.

In order to concentrate up to 99%, it will be possible to use vacuum rectification of water having a 1 to 2% content and compression of the head steam, in order to use it as a heating agent. Consumption

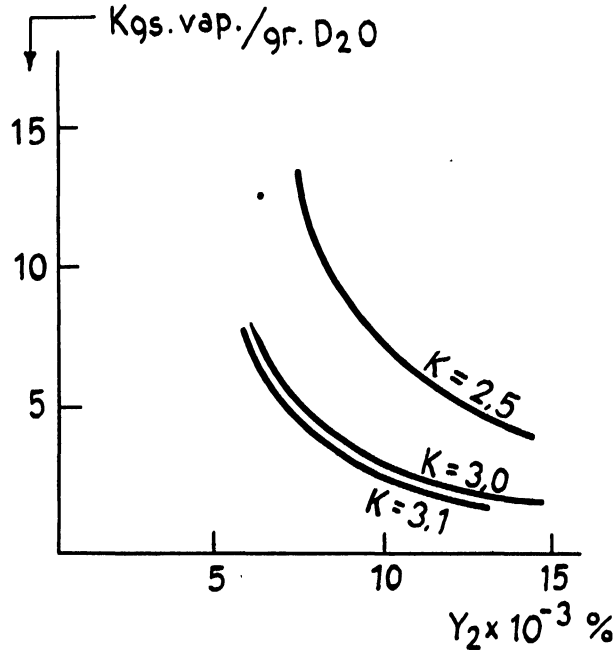

Figure 6

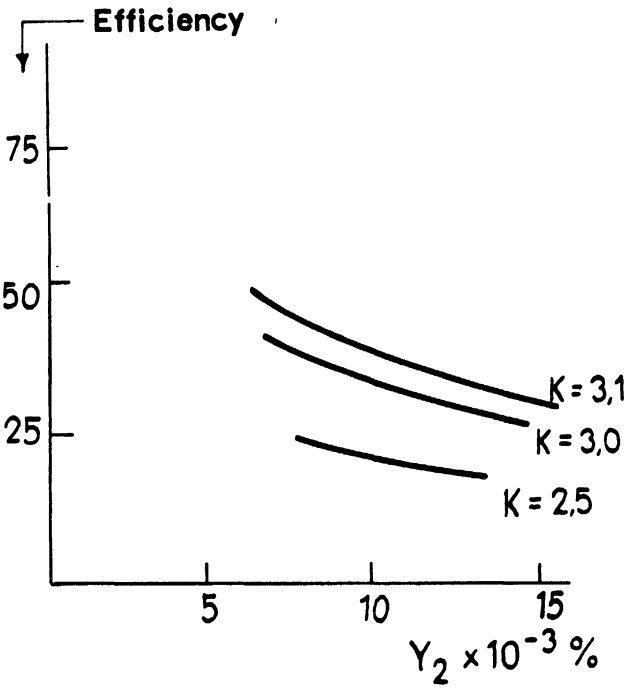

Figure 7

per gm of D_2O in this phase of the process is low, and does not modify the order of magnitude of the values given earlier.

The electrolytic installations having separation factor 6, with burners from the third group on, consume 13 to 15 kwh/gm D_2O with $\eta = 40$ to 45%, and those which have an exchange reaction in the third group, and thereafter burners, (making use of the heat in those to produce the steam required for the exchange reaction) consume 4–6 kwh/gm D_2O with $\eta = 40$–45%. In case the heat of the burners of the first installation is used[2] to produce the steam needed

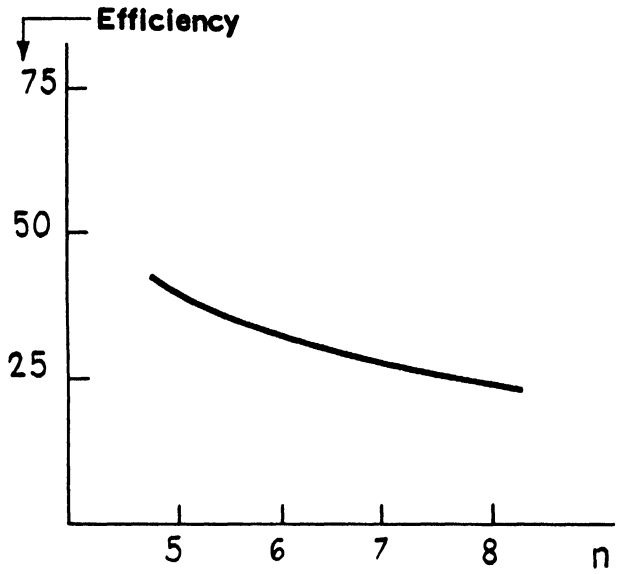

Figure 8

to enrich the feedwater of the electrolytic installation, by vacuum rectification, the consumptions are of the order of 7–10 kwh.

The process suggested by Kuhn de Basilea,[3] which consists of first concentrating the water to 1 part per thousand in electrolytic cells, with rectification under vacuum using a thermal pump to reduce the cost of the steam needed, shows a consumption of 2 kwh/gm D_2O.

The energy consumption in a liquid hydrogen rectification installation[4] is of the order of 6 kwh/gm D_2O (efficiency 90%), if the hydrogen has a deuterium concentration equal to that of natural hydrogen; and, if enriched hydrogen is treated in an electrolytic installation, it may be lower than 2 kwh/gm D_2O with an efficiency of 70%, referred to the feedwater of the cells.

Selak and Finke[5] say nothing regarding the consumption of steam of the Trail installation, but point to operating costs relatively higher than those obtained in the installation under study in this paper. The need for a catalyst in the Trail installation, allowing for the fact that 20% of the cells of the installation proposed show an exchange reaction, is 20 to 30 times greater than those.

Comparing those results, we must allow for the fact that the cost of a kilogram of steam, in the worst possible case (production of steam with electrical energy), is lower than one kwh (approximately 0.75) and that, accordingly, better results can be obtained only with prior concentration by electrolysis and rectification of the hydrogen, or by the Kuhn process, when this is possible.

Naturally, we must allow for the fundamental advantage offered by rectification of the hydrogen, with prior enrichment by electrolysis, giving efficiencies of some 70%.

On the other hand, the numbers chosen were set for a separation factor of 6 and $K = 2$–2.5. As the concentration of D_2O increases, the separation factor also increases, which can also be done by changing the working temperature of the cells. This reduces the steam consumption and the number of groups of cells which are necessary to reach a concentration of 1 to 2%, making the method more advantageous.

Finally, we draw attention to the low cost of installation with respect to all earlier types.

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Infra-Red Methods for the Analysis of Heavy Water

By J. Gaunt,* UK

The accurate determination of the deuterium content of heavy water has been the subject of a number of researches in recent years and methods which have been developed include neutron absorption, interferometric, refractometric and spectroscopic techniques as well as the more conventional density and mass-spectrometric methods. Some of these techniques can be used to cover the whole range of deuterium concentrations from $< 0.02\%$ D to $> 99.5\%$ D with a high degree of accuracy whilst others are accurate only in limited ranges. The majority of the methods developed, however, require delicate manipulation of samples and are time-consuming. Recently a fairly rapid method of deuterium analysis has been developed by Broida[1] who used an electrodeless discharge on water vapour to excite the $H_{2\alpha}$ and $D_{2\alpha}$ emission lines, the intensities of which can be measured spectrometrically. In no case, however, does it appear possible to carry out continuous determinations on flowing streams of liquid water.

As a consequence of the development of modern infra-red spectrometers, infra-red techniques have now found a permanent place in the field of physical methods of analysis. Two important features of such methods are the rapidity with which measurements can be made and the small size of samples required. It is not, therefore, surprising to find an increasing interest in the application of this technique to the problem of the determination of the deuterium content of heavy water.

When the hydrogen atoms of H_2O are replaced by deuterium, although the actual mass difference is small, the reduced mass of the O—X bond is almost doubled, and, since the force constant of the bond is unaffected, the stretching frequency is considerably lowered. Because of this large shift in frequency between the O—H and O—D species it is quite simple to identify infra-red absorption bands which are characteristic of each type of molecule and a basis for analytical methods is readily apparent. Thornton and Condon[2] have reported a method for the 1–5% D range based on the measurement of changes in the intensity of the O—D stretching vibration at 3.98 μ and Trenner and Walker[3] improved the accuracy of the method by the use of thermostatted absorption cells. At the other end of the range, i.e., $> 96\%$ D, Lecomte, Ceccoldi and Roth[4] were able to measure the deuterium content with an accuracy of $\pm 0.1\%$. In this case the measurements were made on a combination band of the HOD molecule at 1.66 μ.

More recently Patterson[5] has carried out an investigation which showed that changes in the concentrations of heavy water in the natural range ca 0.015% D, could be readily observed.

With the development of heavy-water moderated reactors and in view of the plans recently announced of the joint UK-New Zealand scheme to build a geothermal plant to produce reactor-grade heavy water, the need has arisen for accurate and rapid methods of deuterium analysis over a wide range of concentrations both for laboratory and continuous plant monitoring. The results described in this paper are the outcome of investigations which have recently been completed at Harwell to determine whether infra-red methods could be employed for this type of analysis.

99% D RANGE

The accuracy of measurement in the infra-red varies enormously and depends largely upon the specific absorbance of the material under investigation. Although in some ideal cases it is possible to make direct measurements with an accuracy of slightly better than 1%, in many instances this is not so. Consequently for the accurate analysis of heavy water in the 99–100% D range it is impossible to achieve anywhere near the mass-spectrometer accuracy of $\pm 0.01\%$ in D by direct measurement of the D_2O concentration. However, in this concentration region, the equilibrium conditions between the light and heavy water species are such that only HOD and D_2O are present.[6] A small change in concentration of D_2O is, therefore, reflected as a much larger relative change in the HOD concentration. Lecomte *et al. (loc. cit.)* have shown that it is possible to estimate the deuterium content of D_2O in this concentration range by making measurements on the HOD absorption band at 1.66 μ, using 1-cm cells. The accuracy achieved was of the order of $\pm 0.1\%$ of D content. Theoretically, a ten-fold increase in the cell thickness should lead to a ten-fold increase in the accuracy of the estimations. In practice, however, the broadened absorption of neighbouring bands interfere with the measurements and a more suitable region must be found.

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Table I

wt % D_2O (nominal)	Mol. % D	HOD		D_2O		H_2O	
		Mol. %	wt %	mol %	wt %	mol %	wt %
56.00	53.39	49.13	48.95	28.82	30.32	22.05	20.82
54.00	51.37	49.32	49.25	26.71	28.07	23.97	22.68
52.63	50.00	49.36	49.36	25.32	26.65	25.32	23.99
52.00	49.37	49.35	49.38	24.76	26.02	25.95	24.60
50.00	47.37	49.22	49.35	22.76	24.03	28.02	26.62
48.00	45.38	48.94	49.18	20.91	22.12	30.15	28.70

The fundamental absorption band of HOD at 2.946 μ has a very high extinction coefficient and in order to avoid complete extinction the cell length must be small (about 0.05 mm). This leads to a number of difficulties. In the first instance it is difficult to fill and empty a cell of this thickness with accuracy and also since the total volume of liquid contained in it is only of the order of 0.05 ml, a minute trace of absorbed H_2O on the cell windows would lead to a large error in the apparent D_2O concentration. The use of thicker cells would mean that measurements would have to be made at high optical densities with consequent high errors. This can be overcome by using a method of differential comparison in which samples having high optical densities are constantly referred to a standard which has approximately the same optical density. Although absolute measurements cannot be made with accuracy at the high optical densities of either the standard or the samples, the ratios of the samples to the standard can be made with precision.[7] A method of analysis which is based on these principles has been worked out. The cells used are 0.25 mm thick and the working wavelength is 2.946 μ. The method can be applied to either double or single beam spectrometers and is now used at Harwell as the basic analytical method for D_2O analysis in this range.

Although not an absolute method, once a calibration curve has been drawn up, samples can be analysed in approximately 3 mins. The range covered by the method is from 99.5 to 100% and it has been found possible to distinguish between samples differing by only 0.003% D. An example of the repeatibility which has been achieved is given below.

% D estimated	
99.800	
99.799	
99.801	
99.805	Mean = $99.80_0 \pm 0.00_2$%
99.798	cf. Mass spectrometry figure 99.79_9%
99.799	
99.798	
99.799	

50% D RANGE

Although at first sight it would appear impracticable to carry out determination of the deuterium content of heavy-water samples in this concentration range without previous dilution, in practice it has proved to be relatively simple.

When pure H_2O and pure D_2O are mixed, equilibrium is rapidly established according to the equation:

$$H_2O + D_2O \rightleftharpoons 2\,HOD$$

Since the equilibrium constant is known, measurement of one component of this mixture immediately leads to a knowledge of the concentration of the other components. In order to see which component will give the greatest sensitivity in measurement, reference must be made to the absolute composition of the mixture in this concentration range. Using the figures for the equilibrium constant given in reference 6, Table I has been worked out.

From this table it is immediately apparent that the changes in the HOD concentration are sensibly constant over a fairly wide range of deuterium concentrations in this region and the major changes occur in both the D_2O and H_2O species. In either of the latter cases, because of the relatively high concentration of the HOD species, it is not possible to make measurements on either the O—D or the O—H fundamental band. Investigations have shown that the H_2O combination band at 1.445 μ is relatively free from overlapping bands from the other species and could be used as a basis for an analytical method. It was found convenient to use absorption cells 5 mm thick, with glass windows. A differential comparison method was again found to give the greatest precision over a short range of concentrations. The method worked out covers the range from 45–55% D with an accuracy of ± 0.06% D. An example of the repeatability of the estimations is shown below.

% D estimate	
51.82	
51.82	
51.60	
51.74	
51.70	Mean = 51.71 ± 0.06%
51.70	Real value = 51.74% D
51.74	
51.62	
51.62	
51.76	

3%, 0.2% AND NATURAL CONCENTRATION RANGES

When the molar concentration of deuterium in heavy water is less than 4%, the only species present are H_2O and HOD. Changes in the H_2O concentration cannot readily be observed for similar reasons to those already stated for D_2O in the high concentration range and in consequence direct measurement on the HOD species must be made. It has

already been shown that the most suitable region of the spectrum in which such measurements can be made is at 3.98 μ, where the fundamental O—D stretching vibration is observed. The methods of analysis which have been worked out for the three concentration ranges listed above are identical and require simply the use of different cells to cover each range separately. Once again methods of differential comparison have been found to yield the most accurate results but it was also found convenient to use a scale expansion technique in addition. Full experimental details of these methods are being published in a technical paper elsewhere. Typical analytical figures for these ranges are listed in Table II.

Although the analytical methods which have been worked out so far cover only a limited series of ranges, each with a reasonably high accuracy, the technique has not been pushed to its limit and there is little doubt that the whole range from 0–100% D could be covered with the degree of accuracy in determination increasing from about $\pm$ 2% of the deuterium concentration in the natural range to $\pm$ 0.002% in the high concentration range. In every case, the time taken per analysis has been only of the order of 2–3 min, this time being mainly that required to fill and empty the absorption cells. The infra-red technique, therefore, appears to be very suitable for use on continuously flowing streams. At first sight it might appear that to flow samples continuously through the very thin cells required would be extremely difficult and probably would be a major stumbling block in this development. However, it has recently been shown possible using liquids having higher viscosities than water[8] and should not present a real problem. Far more difficult is the production of stable and robust equipment capable of withstanding the rigours of plant-scale operations. Two methods of approach to this problem may be considered: (1) dispersive methods, and (2) non-dispersive methods.

The simplest form that an infra-red analyser can take is one which primarily consists of a source, a narrow-band transmission filter and a detector. Filters having the required characteristics for such work are, in general, not available and some other means must be sought. Savitzky and Bresky[8] have recently described an instrument which uses a non-dispersive method for analysis of a given substance at a given wavelength and which can readily be adapted for the analysis of heavy water. Although optically non-dispersive, the instrument incorporates a selective detector in the form of a variable-diaphragm-type condenser which is filled with a gas which absorbs at the analytical wave-length (e.g., for 2.946 μ, ammonia could be used) and is, therefore, sensitive to changes in the absorption at that wavelength. It is understood that instruments of this type have already proved practicable in continuous plant analyses and appear to be robust and stable.

Alternative to the non-dispersive type of instrument, is the instrument which uses dispersive media for isolating a narrow wavelength band. Woodhull *et al.*[9] have described a plant instrument which uses prisms for dispersion whereas the present author has recently described an instrument which employs a diffraction grating and transmission filters, for use in the laboratory.[10,11] Although this instrument can be used as a fairly high resolution spectrometer, it is best employed as a rough monochrometer and in this manner it has been in use at Harwell for some 12–18 months for the analysis of reactor-grade heavy water. The results which have been obtained with it have been shown to be both repeatable and reliable. Because of the speed with which analyses can be carried out, this method of analysis has now been adopted as a routine.

To transfer an analytical method of this nature from the laboratory to the plant presents a major problem in instrumentation and electronics. This problem has, however, been successfully tackled[8,9]

Table II

Range	*Cell*	*Windows*	*% D estimate*	
2.8–3.6% D	0.07 mm	CaF_2 or Al_2O_3 (synthetic sapphire)	3.23_0 3.24_0 3.23_8 3.24_2 3.23_4	Mean = $3.23_6 \pm 0.00_4$ Real value = 3.23_7% D
0.18–0.27% D	0.18 m	CaF_2 or Al_2O_3 (synthetic sapphire)	0.214 0.217 0.219 0.214 0.215	Mean = 0.216 ± 0.002 Real value = 0.217% D
Natural–0.08% D	0.25 mm	CaF_2 or Al_2O_3 (synthetic sapphire)	0.0355 0.0365 0.0365 0.0365 0.0365 0.0390 0.0375	Mean = 0.0368 ± 0.0008 Real value = 0.0376% D

and instruments have been developed for continuous plant monitoring. Such instruments can be used for the analysis of heavy water and there is little doubt that they can also be adapted to control the flow of a production plant to yield automatically a product of uniform quality.

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Isotopic Analysis of Water by Near-Infra-Red Spectrometry

By Enrique Silberman,* Argentina

The practical difficulties encountered in the determination of the deuterium content of water by the usual methods are well known:[1] density or refractive index measurements require very good purification and careful handling of the samples and where the mass spectrograph is used for analysis, prior decomposition of the water also is required, an operation which has to be carried out with the utmost care in order not to alter its isotopic composition.

This makes the possibility of measurements using the great difference between the absorption spectra of the H_2O, HDO and D_2O molecules in the infra-red most attractive: in fact, the measurements can be made directly on the liquid sample, free from interferences due to impurities unless they are of such a nature that they would strongly absorb radiation in the frequency range of the band used for the analysis, which would be an exceptional situation, particularly with water suitable for nuclear physics experiments.

However, the development and application of these measuring methods are of very recent date. In 1950, Thornton and Condon[2] used the 3.98 μ band to carry out determinations in water containing 0 to 5% D_2O, with an absolute error of less than 0.03%. Samples containing greater concentrations of D_2O had to be diluted down to a measurable range, but the relative error remained under 1% in the 3 to 100% D_2O range. Trenner and Walker[3] gave a detailed description of the technique to be followed to ensure reproducibility of the results. They stressed the need for stabilization of sample temperature, thereby reducing the error to 0.01%. Very recently Gaunt,[4] using the same band, presented a differential method which became independent of temperature variations, guaranteeing an accuracy of 0.0003% in the determination of D_2O concentrations in the 0–0.8% range. The possibility of using the 2.95 μ band for estimation of very highly enriched water is shown in the same paper with a precision reaching 0.003% in samples containing over 99.9% D_2O.

Lecomte, Ceccaldi and Roth[5] introduced a very important simplification of the technique when they tried out bands in the near infra-red, since they offer the following advantages:

1. The use of a spectrograph of simple design and operation, as well as more reasonable price, becomes possible since the expensive and delicate LiF, $CaFe_2$ or NaCl prisms may be replaced by the more common glass prisms; glass may replace CaF_2 in the absorption cell windows and, finally, a PbS detector can take the place of the thermocouple, giving greater sensitivity and affording considerable simplification of the amplifying equipment:

2. Since the bands, in this region of the spectrum correspond to overtones or combinations of the fundamentals, they give weaker absorptions, permitting the use of thicker cells (from 1 mm to several centimeters) thus simplifying the filling, cleaning and thickness measurements of the cells, which are delicate operations when the thicknesses are only some hundredths of a mm as is the case in the rest of the infra-red region. In addition, the effects of the particles accidentally held in suspension in the sample become less important.

The H_2O–D_2O spectrum between 1 and 2 μ shows two main absorption bands (Fig. 1): one in the vicinity of 1.47 μ ascribed to the H_2O molecule; and one at 1.66 μ, ascribed to the HDO molecule.[5,6] After several series of measurements made in order to establish the optimum conditions, Lecomte *et al.* chose the 1.66 μ band, using which they were able to make measurements on mixtures having a D_2O content of over 95% with a precision of 0.1%.

In order to make measurements in other concentration ranges without losing the advantages of the measurement in the near infra-red, we made a point of using the 1.47 μ band. We have succeeded in improving Lecomte's precision, in the concentration range he used, by a systematic study of its characteristics and the introduction of a new generalization of the differential method, and to extend the measurements throughout the whole of the range with a precision that may be adequate for control of an industrial process of D_2O production as well as useful for research purposes. Above all this applies where immediate analyses are needed, as in the case of the study of physical and chemical processes in which the delay due to preliminary processing of the sample, as required by other methods, is not acceptable, or proves impossible with the small thickness required for work at longer wavelengths.

EXPERIMENTAL

The Kipp and Zonen L27 spectrograph of the National Atomic Energy Commission was used with a dense flint prism and a compensated thermocouple (since no PbS detector was available). The original

Original language: Spanish.

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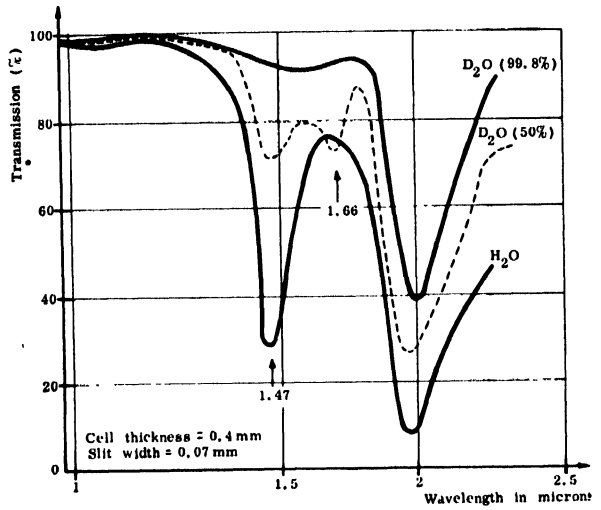

Figure 1

system of photorecording of galvanometer deflections was replaced by another one consisting of:

1. A dc electronic amplifier (Liston-Folb Breaker Amplifier) into which it was possible to inject a low voltage (adjustable) to compensate for zero drift if needed, or shift the position of the zero if desired, as well as low voltages of 1.3, 30 or 100 μv for the purpose of checking.

2. A pen recorder (Speedomax) was coupled to the above amplifier through a filter and voltage divider. In our case, an ordinary filament lamp proved particularly useful as the radiation source, since the wavelength of its maximum emission was very close to 1.47 μ where we intended to make our measurements. The absorption cells were equipped with 1-mm-thick glass windows and lead amalgam spacers of the necessary thickness, except for the cells 10 mm or larger, which were standard cells from a colorimeter.

Thermocouple detection inevitably introduces zero drift, the influence of which, on the accuracy of the measurements, was avoided to a great extent by successively recording for one minute each of the values of interest. During the few minutes taken for such measurements, zero drift is practically constant and it is possible to measure the distance between the lines produced in such a way. In this manner, transmissions of some 40–50% can be determined to 0.5% and when the transmission lies between 80 and 100%, this error may be reduced to 0.25%.

DISCUSSION OF EARLIER METHODS AND DETERMINATIONS

It should be understood that the D_2O percentages mentioned above and quoted in most of the papers to which reference has been made, are those to which the solutions used for comparison had been adjusted by mixing H_2O and 99.8% D_2O. These percentages do not express the molecular content in D_2O since a fraction of these molecules take part in an exchange reaction with H_2O molecules to give HDO; however, the percentage does give a correct indication of the H/D ratio in atoms per cent. Since our measurements are made on a band almost completely due to H_2O, it also is clear that only a part of the H_2O added to the D_2O to prepare the standard solutions remains unchanged and contributes to the changes in absorption, while the fraction transformed into HDO contributes to the intensity of bands situated at other wavelengths where we do not take readings. From this, we deduce that we should not expect compliance with Beer's law and we are, therefore, forced to depend on empirical calibration curves.

In order to obtain some idea of the shape of these curves, we made a preliminary survey covering the whole of the concentration range. We established empirically, the sample thickness that would yield a transmission of 20–80% and found that l (cell thickness) = 0.4 mm. The curve in Fig. 2, which shows optical density $D = \log I_0/I$ as a function of the concentration is, within experimental errors, a straight line for deuterium contents up to 60%, and departs from linearity toward greater optical densities with higher D concentrations. This curve may be useful for several purposes:

1. It is a calibration curve for the determination of the deuterium content of solutions of D_2O in H_2O, regardless of concentration. Although, in Equation 1:

$$D = k \times c \times l \qquad (1)$$

k is not constant for $c < 40\%$, it may be considered constant over small concentration ranges, its value then being expressed by the slope of the curve. Then Equation 1 gives as absolute error for the determination of c from a measurement of D, of:

$$\Delta c = \frac{1}{k \times l} \epsilon_{I_0/I} \qquad (2)$$

in which $\epsilon_{I_0/I}$ is the relative error which can be made

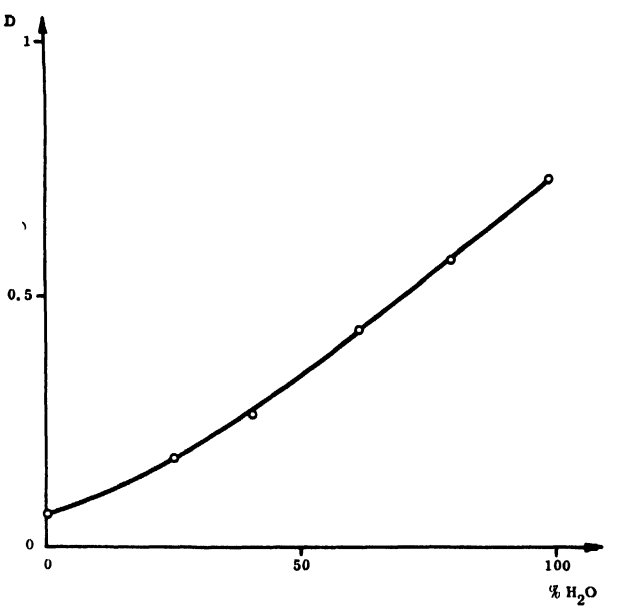

Figure 2

in measuring I_0/I. In our case, the application of Equation 2 leads to values of Δc between 0.5 and 0.7%, with the lower value corresponding to concentrations of some 50% for which the thickness taken for the sample is optimum. This precision should be sufficient for control purposes, which may be made easily, automatically and continuously over the intermediate ranges (5 to 95%) obtained in an industrial heavy water manufacturing process.

2. The curve gives us values of k with which the sample thickness required for any concentration may be computed, by means of Equation 1, in order to obtain predetermined transmission rates, a very useful item for the more exact estimation of water of approximately known deuterium contents.

3. By correlating the curvature obtained with the H_2O, HDO and D_2O concentrations effectively present, even though we identify the sample by its total D or H content, we postulate that it is possible to reach some conclusions on the effective contribution of each of the fundamental vibration modes of the three molecules to the intensity of the band, a point on which the existing publications[5,6,7,8] are not in good agreement.

In order to improve the precision of the determinations over small ranges, the scale should be increased, thus reducing $\epsilon_{I_0/I}$. This can be done in two ways: amplification can be increased to the limit imposed by the signal-to-noise ratio of the equipment, or the signal alone (and not the noise) can be made more intense by increasing the slit widths. In such a case, the limit arises from the reduction in the percentage absorption due to the greater spectral width falling on the detector. In effect, this will average the absorptions over this width and give values consistently smaller than those corresponding to the narrow frequency interval taken at the maximum of the band. For this reason, its shape now becomes of interest to us. In order to determine it, we made a second preliminary experiment, measuring the transmission percentage for several slit widths. From the curve so obtained (Fig. 3) it can be seen that we are dealing with a rather wide band, and that slits up to 0.4 mm may be used without appreciably reducing the absorption, thus giving signals 10 times more intense than those corresponding to the 0.15 mm slit used in the first experiments.

By increasing the signal in this manner, we are now faced with the problem that it is not possible to record on the same chart, the zero value (radiation off), the total radiation (I_0) and the radiation transmitted by the sample (I). We used a differential method for this.

Solutions of two strengths, c_1 and c_2, were prepared, corresponding to the ends of the narrow range in which we intended to make measurements. Zero being off the chart (Fig. 4), the signals were amplified, until the I_1 and I_2 readings appeared at the opposite ends of the scale. The difference $\Delta I_0 = I_2 - I_1$, will be proportional to total radiation I_0 and

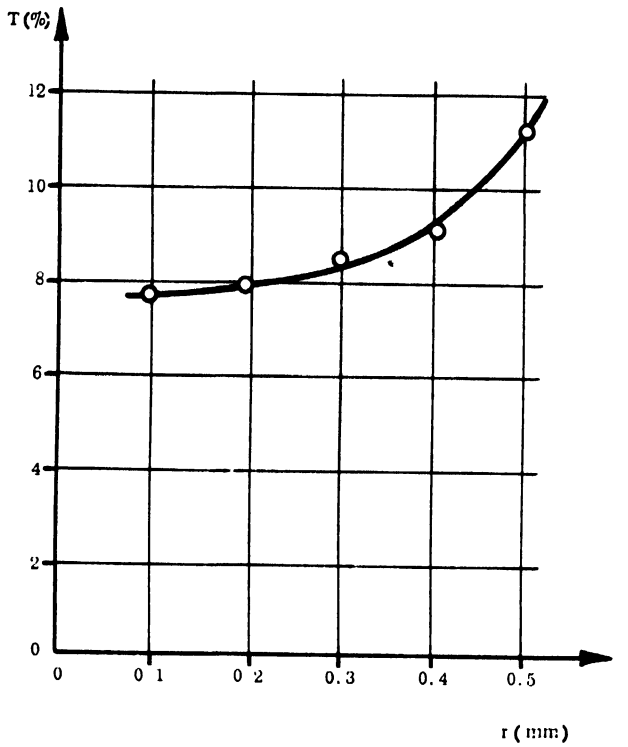

Figure 3

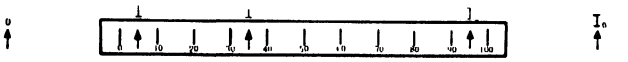

Figure 4

to a certain function of the concentration difference $\Delta c_0 = c_2 - c_1$, or:

$$\Delta I_0 = I_0 \times f(\Delta c_0) \qquad (3)$$

Under these conditions, a sample showing an intermediate concentration, somewhere between c_1 and c_2, will give a reading somewhere between I_1 and I_2; the difference $\Delta I = I - I_1$, being again proportional to I_0 and to the same function of the concentration difference $\Delta c = c - c_1$, or

$$\Delta I = I_0 \times f(\Delta c) \qquad (4)$$

The value of $\Delta I/\Delta I_0$ will be independent of I_0, being only a function of c_1, c_2 and c. Since c_1 and c_2 are known, the following calibration curve may be drawn.

$$\frac{\Delta I}{\Delta I_0} = \phi(\Delta c) \qquad (5)$$

If the substance obeys Beer's law (in the interval $c_1 - c_2$) Equation 5 will become:

$$\frac{\Delta I}{\Delta I_0} = \frac{1}{1 - e^{-k \times l \times \Delta c_0}} \cdot (1 - e^{-k \times l \times c_0}) \qquad (6)$$

For a small Δc_0, using the first term of the exponential series development, we have:

$$\frac{\Delta I}{\Delta I_0} = \frac{\Delta c_0}{\Delta c_0} \qquad (7)$$

and, in other words, the curve of Equation 5 will be a straight line and the measurement is limited to a linear interpolation.

If it is necessary to make a large number of determinations in the same concentration region, solutions c_1 and c_2 may be replaced by suitable filters (darkened or ground glass, steel mesh, etc.) which have transmissions approximately the same as those of the solutions, and which are usually more stable and easier to handle. The above reasoning holds for the empirical calibration; from Beer's law, if the first filter transmitted $I_1 = \alpha I_0$ and the second $I_2 = \beta I_0$, the corresponding Equation 6 becomes:

$$\frac{\Delta I}{\Delta I_0} = \frac{1}{1 - \beta/\alpha}\left(1 - \frac{1}{\alpha} \cdot e^{-kcl}\right) \qquad (8)$$

If c varies within a small interval, one may deduce from Equation 8 that $\Delta I/\Delta I_0$ will also be a linear function of c.

Using this differential method, the errors made in the determinations may be reduced whenever it is possible to increase the signals, either by widening the slit (provided this does not affect the absorption coefficient), or increasing the amplification. With our equipment, which permits the reproduction of 0.25 divisions on a scale of 100 units, the error would be of the order of 1/400 of the difference in concentration corresponding to signals at the opposite ends of the scale.

RESULTS

1. Samples Containing over 95% D_2O

The 1.47 μ band is particularly useful in this concentration region. Using 10-mm cells and 0.4-mm slits, and amplifying until a full scale deflection equivalent to 2 μv was obtained, the signals for 99% and 99.8% D_2O solutions are found to be 80 divisions apart. In this case, the zero is off the scale and in fact, the total signals measured are approximately 40 μv. The noise in our system, which increases with the signals, is increased so that only ½ division accuracy may be assured, a condition which corresponds to $\Delta c = \pm 0.005\%$ (Fig. 5).

2. Samples with Less than 5% D_2O

With a 1-mm cell and the same slit and amplification as above, the signals obtained for normal water and 5% D_2O would be 25 divisions apart. Now the signals are weaker (5 μv), but the same condition applies to noise, and ¼ division may be obtained corresponding to a $\Delta c = \pm 0.05\%$, (Fig. 6).

APPLICATIONS

We noted that: (1) the maximum emission of an ordinary filament lamp is at about 1.5 μ, and decreases rapidly toward longer and shorter wavelengths; (2) heavy water has a good transmission without any important bands from the visible to 2 μ; and (3) ordinary water has a strong absorption band at 1.47 μ and transmits very little beyond 2 μ.

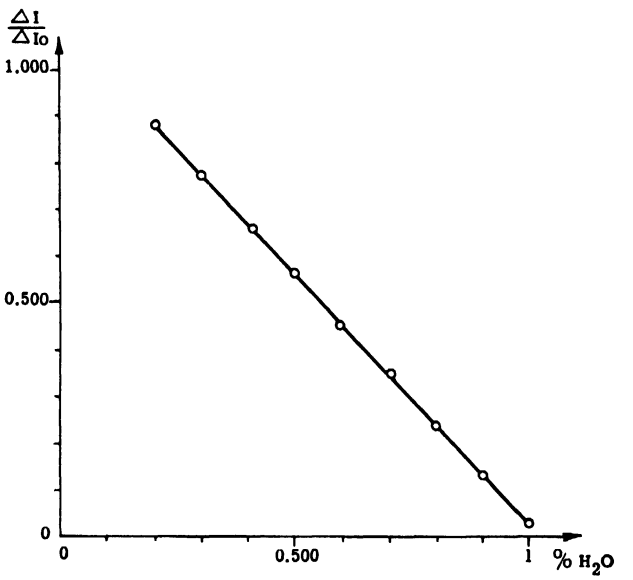

Figure 5

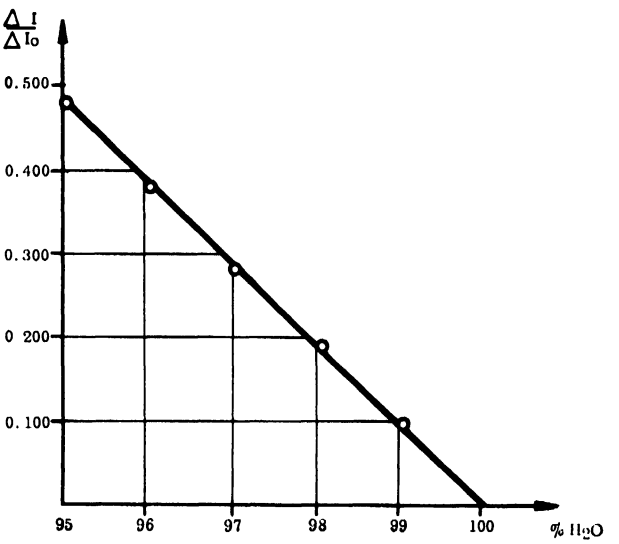

Figure 6

This means that there will be a substantial difference between the radiation emited by a lamp after passing through identical cells containing H_2O and D_2O respectively. These differences may be increased by the use of suitable filters. On the basis of these data, we have made a continuous analyzer as sketched in Fig. 7. The system may be improved by the use of PbS detectors, modulation of the beam, ac amplification and recording devices. Design is still in the early stages of development but preliminary results indicate that it is possible at least to make very simple units which, operating as null-point instruments, could actuate servo systems in such a way as to automatically maintain uniformity of the concentration of the liquid flowing through the pipe systems of a plant used for industrial production of D_2O.

CONCLUSIONS

With the equipment available, estimations can be made with a precision varying from 0.05% for water

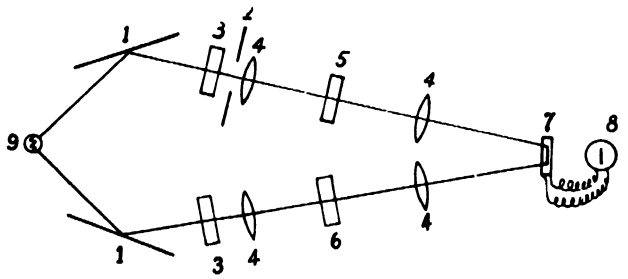

Figure 7. Analyzer: (1) plane mirrors; (2) iris diaphragm; (3) filters; (4) convex lenses; (5) cell containing reference solution of D_2O; (6) cell containing sample; (7) two thermocouples connected in opposition (Moll and Burger thermorelay); (8) galvanometer; (9) filament lamp

very rich in D_2O to 5% in water containing only 1% D_2O. Where standard solutions are available for calibration checking, a complete measurement can be carried out in 5 minutes. With better equipment, namely with higher signal-to-noise ratios and zero-drift elimination, errors can be lowered from the values mentioned and measurement time decreased.

Compared with other methods, the fundamental advantage of the technique offered is that it makes direct analyses of liquid samples possible without the need of extensive preliminary treatment. In addition, the samples may be small (from 0.1 to 2 ml) and are recovered intact. As regards measurements in the far infra-red, the proposed band has the merit of allowing the use of more readily available instruments, and of simplifying the techniques by the use of thicker cells and the elimination of windows requiring careful handling.

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On Methods of Isotopic Analysis of Heavy Water

By K. W. Vladimirsky, M. Y. Katz, B. M. Stasyevich, USSR

Several methods have been proposed for the determination of the isotopic composition of a mixture of D_2O and H_2O. These methods are based on the difference of certain physical properties of heavy and light water or deuterium and hydrogen. The most widespread are the methods based on density measurement: the pyknometric, drop, and float methods. These methods are simple, they do not require complex apparatus and highly qualified workers and they give a high degree of accuracy. A drawback in the density method is the possibility of systematic errors in the determination of the isotopic composition which are connected with inaccuracies in the determination of the basic calibration constant—the density of isotopically pure deuterium oxide.

The aim of the present work is the determination of isotopically pure deuterium oxide. Aside from the absolute measurements of the density of the pure product, parallel measurements of the density and isotopic composition were conducted. Measurements of isotopic concentrations were made by methods of nuclear magnetic resonance and mass spectrometry.

OBTAINING HEAVY WATER WITH A MAXIMUM CONCENTRATION OF DEUTERIUM AND DETERMINATION OF THE DENSITY

Two identical metal (stainless steel) filled rectification columns of height 2 m and inside diameter 20 mm (arrangement L and arrangement M) were constructed to obtain heavy water with a maximum concentration of deuterium. Figure 1 gives a cross-sectional view of the arrangement.

A differential mercury pressure gauge showed the difference in pressure in the boiler (*1*) and condenser (*6*), i.e., the column resistance. The filling (h = 2 mm, $\phi = 1.5$ mm) of the column was made of a nickel net (1500 holes per cm^2).

3700 gm of heavy water were poured into arrangement *1*.

The heavy water was obtained electrolytically and had a concentration of 99.56% deuterium and 0.35% heavy isotopes of oxygen; arrangement M was supplied with 3550 gm of heavy water obtained by distillation, with a deuterium concentration of 99.67% and 1.2% of heavy isotopes of oxygen.

In this work the rectification column was used as an instrument serving to extract the light components of the product poured in, and thus obtaining the most concentrated final product. In the separation process the column was closed. For a certain period of time (one cycle) the column worked without sample selection. At the end of each cycle, the liquid, enriched with the light isotope of hydrogen was drained out of the collector. The concentration of deuterium in the system rose. A cycle of continuous operation of the column lasted 120 hours, after which the liquid was drained from the collector and analyzed: the column was flooded and was then brought into normal operation with a new cycle. A total of 18 cycles

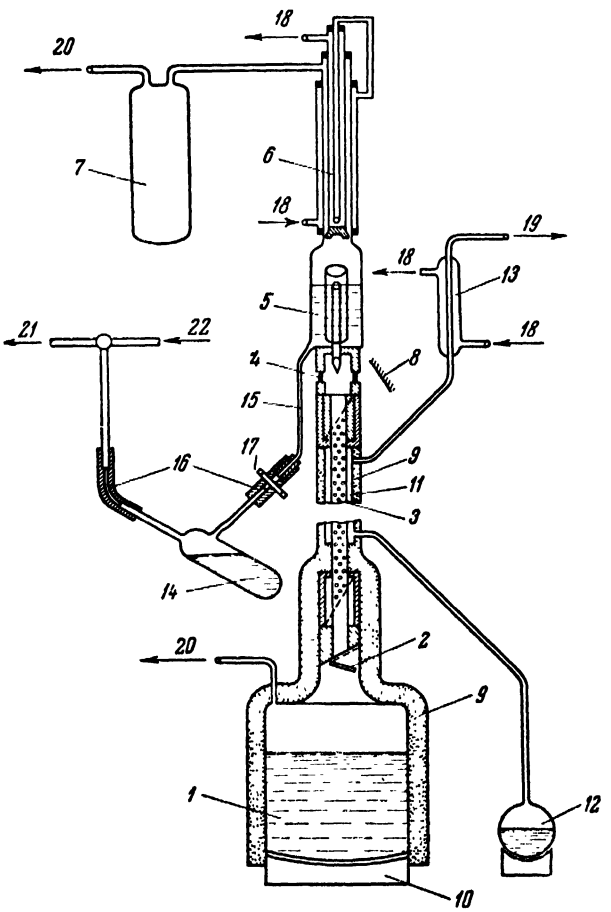

Figure 1. Scheme of rectification column: (1) boiler; (2) valve; (3) column; (4) glass windows; (5) mixer and collector; (6) powerful condenser; (7) glass flask protector; (8) mirror; (9) heat insulation; (10) electric boiler heater; (11) column heating jacket; (12) boiler; (13) condenser; (14) glass flask for taking samples; (15) metal capillary (ϕ = 1 mm), (16) vacuum rubber connections at joints; (17) clamp; (18) coolant feed; (19) connection with mercury lock; (20) connection with mercury differential pressure gauge; (21) connection with vacuum pump; (22) connection with dry air

Original language: Russian.

were conducted with the arrangement *L*, and 17 cycles with the arrangement *M*.

The densities of the samples taken during operation of the column were measured by the differential pyknometric method. Ordinary Moscow water was used as control.

Measurements were taken at 25°C. The isotopic composition of oxygen in the samples was reduced to standard by a reaction of isotopic exchange with dried natural carbon dioxide, at a pressure of 70 atm and a temperature of 90°C. Water purification was done in a quartz apparatus. Each sample was boiled under reflux in the presence of $KMnO_4$, and three times distilled with separation of 10% of the initial and final fractions.

Figures 2*a* and 2*b* give the densities of samples from the collectors and boilers for the last cycles of the arrangements *L* and *M* respectively. It may be seen from the graphs that the sample densities for each arrangement taken from the collector and boiler in the last cycles coincide with measurement errors (± 0.00001). Enrichment in each arrangement was of the order of 6–8, therefore it may be considered that the concentration of the product in the boilers in the final cycles was of the order of 99.999%.

Measurements conducted on samples taken from the boiler were used to determine the density of isotopically pure heavy water:

Cycle number	*Sample density* d_{25}^{25}*
Arrangement L	
L–16	1.107694
L–17	1.107690
L–18	1.107699
Average arrangement	1.107694
Arrangement M	
M–14	1.107686
M–15	1.107708
M–16	1.107677
M–17	1.107679
Average arrangement	1.107688
Average from both arrangements	1.107691

* The value d_{25}^{25} is a ratio of absolute density of heavy water at 25°C to normal reference water at 25°C.

The value of d_{25}^{25} obtained is the mean value from 56 density measurements. The error in this figure due to accidental measurement errors does not exceed ± 0.00001. The following corrections must be introduced into the value obtained: corrections for incomplete enrichment of the product in the column, for the difference from the standard of the isotopic composition of oxygen in the samples, and for the distillation effect during purification of samples.

The sum correction is $+ 8 \times 10^{-6}$. The density value of isotopically pure heavy water could, on the basis of these measurements, be taken as

$$d_{25}^{25} = 1.10770 \pm 0.00001$$

THE NUCLEAR MAGNETIC RESONANCE METHOD

The method of isotopic analysis utilizing nuclear magnetic resonance is based on the difference of the magnetic moments of the nuclei of hydrogen and deuterium, which makes it possible to measure the amplitude of the resonance of hydrogen and deuterium without mutual interference and ensures the absence of systematic errors in saturated concentrations, for example, in the case of the concentration of deuterium close to 100%. In the absence of one of the isotopes the experimentally determined amplitude of the respective signal is equal to zero, accurate to accidental errors of measurements, which errors are determined chiefly by the fluctuating noise of the input cascades of the apparatus used.

Measurements of isotopic concentrations are conducted by a relative method, by comparison of the amplitudes of the signals from the standard sample and the sample being investigated, which samples are of identical chemical composition. Obvious considerations demand the measurement of the signal amplitude corresponding to an isotope, the concentration of which is less in the sample.

For conducting measurements using a magnet with a negligible non-uniformity of field, the accuracy of measurement is determined only by the magnitude of the noise and the degree of the constancy of amplification in the recording apparatus. If widening due to non-uniformity of the magnetic field is commensurate with the natural line width, interference of signals from various parts of the samples arises, which considerably increases the dependence of the measured results on the geometry of the instrument and reduces the measured accuracy. Control experiments showed that for good reproducibility it is sufficient for the experimental line broadening to be several times less than the natural width. The natural line width is changed in a wide range depending upon the chemical composition of the sample; for protons in water it is of the order of 0.1 cycle per second. The conducting of measurements with a line of such a small width would require a uniform field in the main body of the sample, with an accuracy of the order of a fraction of a millioersted. In order to avoid

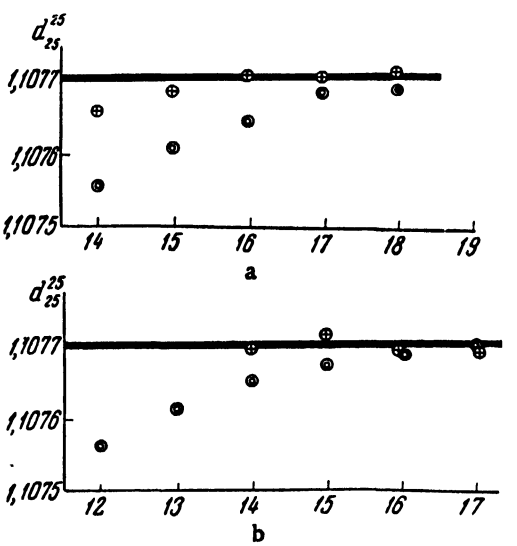

Figure 2. Densities of samples from collectors and boilers for last cycles: (a) arrangement L; (b) arrangement M: samples from boiler; samples from collector; numbers of cycles are plotted on abscissa

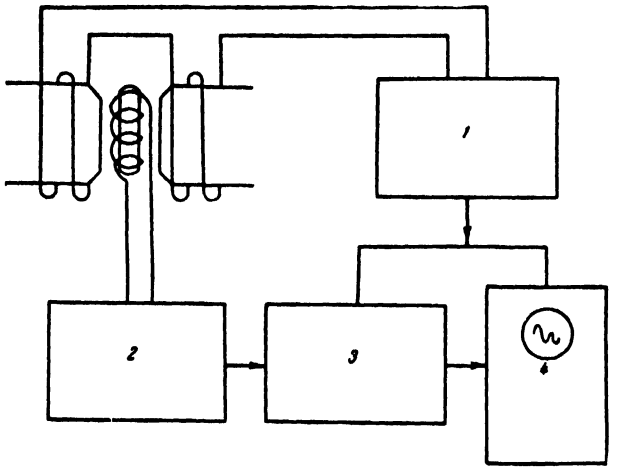

Figure 3. Block scheme of equipment for measuring signal amplitudes of nuclear magnetic resonance: (1) audio-frequency generator; (2) generator, detector, amplifier; (3) synchronous filter; (4) cathode oscillograph

this, measurements of the signal amplitudes were conducted on samples which contained paramagnetic salts that increase the natural linewidth to values that are in accordance with the degree of the field uniformity of the magnet being used. In order to obtain satisfactory results in this case, field uniformity in the main body of the sample of the order of 0.1 oersted is sufficient.

The use of paramagnetic salts for increasing the self-broadening of the line also simplifies to a great extent the dependence of the signal amplitude of nuclear magnetic resonance on isotopic concentration. For diamagnetic liquids, e.g., for pure water, this dependence may prove to be nonlinear, since aside from the trivial proportionality between the number of nuclei of a given isotope in the sample and the signal strength, the latter may depend upon the isotopic concentration also because of changes in relaxation times. In aqueous solutions of paramagnetic salts, the basic mechanism of establishing thermal equilibrium is the interaction of the magnetic moment of the nuclei with the considerable greater moments of the paramagnetic ions. This interaction does not depend on isotopic concentrations. The signal amplitude in this case is strictly proportional to the concentration throughout the whole range of changes in isotopic concentration.

The apparatus designated for analytical purposes should ensure, aside from high sensitivity, stability of instrument readings in time and constant graduation of the instrument when samples are changed.

Most important for constant instrument readings is the selection of the input cascade scheme. Schemes making use of high-frequency compensation (the block scheme and bridge schemes) are only slightly fitted for analytical purposes. Instruments of this type register a certain mixture (depending on regulation) of the signals of dispersion and absorption. Compensation disturbances taking place as a result of temperature variation of the instrument and, in particular, when the samples are changed, change greatly the form and amplitude of the signals. We used instruments without compensation. The coil into which the sample was placed was directly connected with a detector. High-frequency voltage was fed from an external generator. Instruments of this type (when the circuit is brought into resonance with the frequency of the external generator) register absorption without the admixture of the dispersion signal and make it possible to obtain a reproducibility of signal amplitudes sufficient for analytical purposes. The sensitivity of the apparatus used in this work makes it possible to determine the hydrogen content in concentrated heavy water with an absolute error not exceeding 0.01%.

The above mentioned absence of systematic errors in the region of small isotopic concentrations make it possible to use this method for determining the density of isotopically pure heavy water. 0.1*M* solutions of $CuSO_4$ in heavy water with various concentrations of deuterium including two solutions in heavy water of highest possible concentration were prepared for measurements.

The isotopic composition of oxygen in heavy water was preliminarily reduced to standard by isotopic exchange with CO_2. From the initial solutions, 9 samples of 4-cm volume were prepared, which were used for measurement of signal amplitudes of nuclear magnetic resonance. The dissolved $CuSO_4$ played the role of a paramagnetic catalyst in the measurements ensuring optimum measurement conditions. The same initial solution was subjected to standard purification and was used for measuring the density by the differential pyknometric method. The density of the isotopically pure heavy water was determined by linear extrapolation of the results to a zero concentration of hydrogen.

Safety measures were taken while filling the ampoules and making the density measurements. The purpose of the measures was to reduce the dilution of the samples by natural water.

$CuSO_4$, repeatedly recrystallized from concentrated heavy water, was used for preparation of solutions and this made it possible to obtain solutions with a small content of the light hydrogen isotope and thus to improve the results of extrapolation to zero concentration of the light isotope. The small quantities of the light isotope that were introduced with the water of crystallization were automatically taken account of in further measurements and were not therefore a source of errors.

For measurements of signal amplitudes of nuclear magnetic resonance, use was made of narrow-band systems of two types; the synchronous filter[1] and the synchronous (phase sensitive) detector. The corresponding block schemes are given in Figs. 3 and 4. Amplitude modulation of the magnetic field (which amplitude exceeded considerably the width of the resonance line) was used in the case of the synchronous filter. The resonance line was observed, with the aid of the cathode ray oscillograph, in the

form of a narrow peak accompanied by damped oscillations.[2] Measurements were made of the difference of the ordinates of the first maximum and the minimum of the oscillogram with the aid of a calibrated potentiometer in the circuit of the vertical sweep of the cathode ray oscillograph. In making measurements with saturated solutions the signal/noise ratio at the input of the synchronous filter was considerably less than unity; the use of the synchronous filter made it possible to raise the signal/noise ratio to a value of the order of five.

Measurements with the synchronous detector were carried out in the usual way. The signal was registered on a recorder. Both methods produced results that coincided within the experimental error.

The results of one of a series of measurements relating to four initial solutions are given in Fig. 5, where the averaged density values are placed on the X-axis and the values, obtained by separate measurements of the hydrogen concentration (in arbitrary units) are plotted on the Y-axis. The averaged results are given in the following table:

d_{25}^{25}	*Hydrogen concentration (in arbitrary units)*
1.107637	0.230
1.107632	0.234
1.107362	0.987
1.106881	2.250

Normalization of the measurements gave the following result:

$$d_{25}^{25} = 1.10772 \pm 0.00001$$

THE MASS SPECTROMETRIC METHOD

For the mass spectrometric analysis of water it is best to introduce into the mass spectrometer a gaseous mixture of deuterium and hydrogen in which the concentration of D and H corresponds to the concentration of D and H in the water being analyzed. In the mass spectrometer designed for analyzing heavy water having a high concentration of deuterium, the ions of mass 3 and 4, accelerated by a constant potential, on leaving the ion source enter the magnetic analyser. The permanent magnet has pole pieces which are made in the form of a sector with the apex angle equal to 30 degrees. At its input, the instrument has two collectors, which permit simultaneous registration of currents of D_2^+ and HD^+ ions. The ratio of the ion currents is measured with the aid of a compensation set.* The concentration of deuterium in the water being investigated is calculated from the measured ratio of the ion currents.

The design of the mass spectrometric setup has the following peculiarities:

1. The tube of the instrument may be heated to a temperature of 500–600°C and the vacuum system to 350°C.

2. The special design of the ion source permits measurements being made by the two-filament method, which ensures exclusion of discrimination effects due to the hot filament.

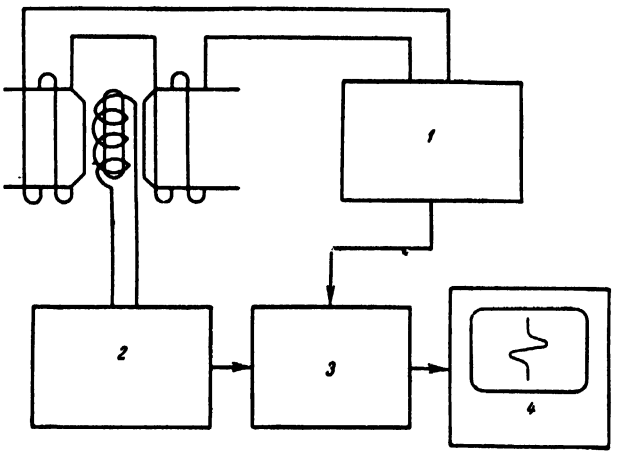

Figure 4. Block scheme of equipment for measuring signal amplitudes of nuclear magnetic resonance: (1) audio-frequency generator; (2) generator, detector, amplifier; (3) synchronous detector; (4) self-recorder

The gaseous sample was prepared for analysis of heavy water by the isotopic exchange method of the following reactions:

$$D_2O_{liq} + HD \rightleftarrows HDO_{liq} + D_2$$

The equilibrium constant of this reaction is $K = 3.33$ at 25°C. Platinum black was used as catalyst. Conditions ensuring a complete exchange reaction were investigated experimentally; sample preparation procedure ensuring 0.01% measurement accuracy for the concentration of deuterium was worked out. Concentrations of deuterium and hydrogen in the heavy water being analysed are computed on the basis of the measured ratio of ion currents

$$\alpha = I_{D_2}/I_{DH}$$

$$D_2O_{liq} + H_2O_{liq} \rightleftarrows 2HDO_{liq}$$

$$D_2O_{liq} + HD \rightleftarrows HDO_{liq} + D_2$$

The total error in determining the concentration of deuterium in heavy water is made due to errors in the value of α and the error of exchange reaction and equilibrium is 0.01–0.02%.

A number of corrections were introduced into the measured value of α.

1. Correction for instrumental resolving power. This correction was determined during each measurement from the mass spectrogram. It was + 0.02% of the deuterium concentration being measured.

2. Correction for the dependence of the ratio of ion currents upon the filament of the ion source. It was found experimentally that the necessity for introducing this correction was caused by the catalytic action of the hot filament, which brings about an intensive exchange of the gas in the molecular flow with the gas adsorbed on the internal surface of the instrument.

* This set coincides, in its main part, with Nier's set published in 1947.[3]

The presence of two filaments in the ion source made it possible to determine the value of this correction experimentally. This correction in an instrument well freed of hydrogen is + (0.01 ÷ 0.005%) of the concentration of deuterium being measured.

3. Correction for formation in the ion source, of ions different from D_2^+ and HD^+.

In measuring a gas with a concentration of deuterium that exceeds 99%, only ions of mass 6 and 2 (D_3^+ and D^+) are of importance. It was possible to estimate this correction by direct measurement of the peak intensities of these masses. The value of this correction is + (0.01 ÷ 0.05%) of the concentration of deuterium.

A modified procedure for mass spectrometric measurements was used to determine the density of 100% heavy water.

Heavy water samples were taken from the pyknometer in which their densities were determined, in special ampoules. The ampoules were preliminarily degassed in a high vacuum (10^{-5} mm Hg). The thin end of an evacuated ampoule was broken inside the liquid.

The gas used for isotopic exchange contained 99.75 ± 0.01% deuterium. This same gas was used to clean the instrument before each analysis. The cleaning was continued until a constant value of α (5-8 days) was obtained.

Measurements of the densities and concentration of deuterium were made on four samples of heavy water. The results of these measurements contain all necessary corrections and are given in the following table:

d_{25}^{25}	C_D in %
1.107637	99.90 ± 0.01
1.107586	99.85 ± 0.01
1.107362	99.65 ± 0.02
1.106881	99.16 ± 0.02

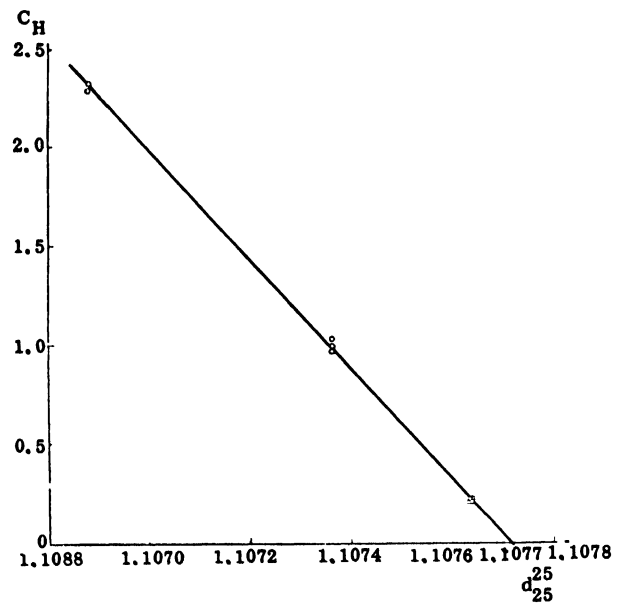

Figure 5. Extrapolation to zero concentration of the results of a series of measurements of hydrogen (nuclear magnetic resonance method): C_H = hydrogen concentration in arbitrary units

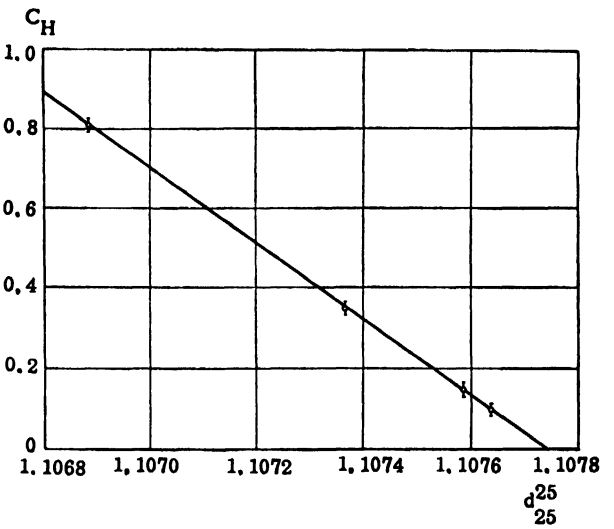

Figure 6. Extrapolation of results of measurements to zero concentration of hydrogen (mass spectrometric method); C_H = hydrogen concentration in percentage

Using these values, linear dependence between density and concentration was obtained by the method of least squares. This dependence is shown in Fig. 6. Extrapolation of the linear dependence obtained to 100% concentration of deuterium gives the following values of the density of 100% heavy water.

$$d_{25}^{25} = 1.10774 \pm 0.00002$$

CONCLUSION

The table on this page gives a comparison of the density measurements of isotopically pure D_2O carried out by different investigators in the course of the last ten years.

An analysis of these data make possible the following conclusions:

1. The results obtained by methods utilizing determinations of isotopic concentrations, the determinations being independent of density measurement, agree within the limits of experimental error.

2. The result obtained by the method limited to measurements of densities is 0.002 ÷ 0.004% below the results obtained by other methods, which is apparently connected with the use of a product with an unmeasured concentration of deuterium.

3. The differences between the results obtained by various methods may easily be explained if we take account of the fact that the main source of systematic errors is the dilution by natural water during measurement operations and in the process of preparing a saturated concentration sample.

In the method that is limited to density measurement dilution of the sample may lead only to a reduction of the measured value of d_{25}^{25}.

Dilution of the sample during the filling of ampoules that are used for measuring the signal amplitude of nuclear magnetic resonance is apparently negligible. The basic source of systematic errors is dilution of the samples during density measurement,

which may lead only to a reduction of the measured value of d_{25}^{25}.

In the method that makes use of the mass spectrometer, dilution of the sample during measurement may lead only to an increase in the measured value of d_{25}^{25}.

4. In the measurements conducted by the density method and the mass spectrometer method, an accuracy close to the possibility limits of these methods has been obtained.

In the method which used nuclear magnetic resonance, the source of systematic errors may be reduced considerably if measurements of density and hydrogen concentration are made on the same samples, making use of a pyknometer filled with a sample of heavy water. However, for this purpose it is necessary to work out a method of measuring the signal amplitudes of nuclear magnetic resonance on samples of heavy water that do not contain paramagnetic catalysts.

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The Distribution of Isotopes in Some Natural and Industrial Waters of Yugoslavia

By L. Knop, Yugoslavia

Following the papers of Ruber,[1] Wirtz,[2] Lamb and Lee,[3] Hall and Jones,[4] Richards,[5] Vukanovic and Pavlovic,[6] we tested the pyknometer, the magnetic float and the temperature float methods. The last two were preferred. The magnetic float was designed for our own use, but it was of a much modified design compared with those referred to in older papers. A 5–mm long and 0.7–mm thick, strong permanent magnet was sealed in the quartz float. The volume of the best float was 0.1 ml. Its weight was adjusted for the temperature interval of 20–21°C by careful etching with hydrofluoric acid. The sample tube, in the shape of a test tube, was made of quartz and provided with a closely fitting stopper. The tube was calibrated for one ml samples and kept in an air thermostat which was controlled from outside by water at constant temperature. A temperature constancy of 0.002°C was achieved. The electric current flowing through an electromagnet below the sample tube was measured. The current was so adjusted that the float, set at a fixed mark, just began to rise again. In constructing the apparatus great care was taken to center the position of the sample tube in the thermostat, and all ferromagnetic parts were eliminated. Single measurements gave a deviation of ± 1.4 γ density units. Some disturbances in measurements were seen to be produced by strong magnetic and strong electric machines which were located 10–20 m away. Precision work with the float could be achieved only when the machines were not operated. These disturbances did not occur in our work with the temperature float which was designed for larger samples and developed after the papers mentioned above and after those of Lewis and McDonald,[7] as well as after the papers by Emeleus and co-workers.[8] Some alterations were made in the design of the apparatus, and it was adjusted to suit our working conditions. The graduated 3-ml quartz sample tube was not immersed in the water thermostat. Water in a Hoeppler ultrathermostat was constant only to ± 0.01°C which was, however, too low for our requirements. Water was circulated through two tubes into a well insulated vessel. A double-walled cylinder, filled with water, was placed inside it, in such a manner that the water was heated only by the air between the two vessels. The sample tube and float, a Beckmann thermometer, a glass heating or cooling coil and a slow-speed stirrer were immersed in the water of the inner cylinder. Owing to the layer of air between the two vessels of water it was possible to maintain a temperature constant to ± 0.001°C. There was, however, one disadvantage that a single measurement took too much time. The changes of temperature of the sample were slow and it took too long to reach equilibrium. In order to shorten this time, a new tube was introduced, which led small portions of the thermostat water directly into the heating coil of the inner cylinder until the desired temperature was reached. Then the pipe was closed and after a short equilibration time the new temperature remained constant for a very long time. To reduce the individual error, two or more thermometers were observed.

Experiments were to made construct the float and the sample tube of less expensive materials. In the development period a float of Pyrex glass was used for 160 measurements over a period of 5 months. This number includes 49 check measurements of the flotation temperature of the float in our standard water, i.e., rigorously and uniformly purified city tap water. During this period a rise in flotation temperature of 0.038°C was detected. This means a decrease of 8 γ and a proportional error of $-0.05\ \gamma\ d$ from one analysis to another. This was intolerable, so all Pyrex and other kinds of glass were rejected.

Quartz proved much better, so we used it for the redistillation apparatus, for the float and for the sample tube. A quartz float of 0.2 ml volume showed, during the first 8 days, a decrease in weight of 1.2 γ established by 15 analyses. This means the average loss of $0.08\ \gamma\ d$ per single analysis. Further use of the same float gave a much lower loss per analysis, which was $0.008\ \gamma\ d$ in spite of necessary and repeated washing in strong chemicals such as hydrochloric, nitric and chromic acid.

The analyses of water samples were taken at a temperature interval of 20.7° to 20.9°C. The real floating temperature of a specific sample was obtained by graphical methods from six successive single measurements of small rise or fall velocities of the float. The motion of the float was observed by means of a cathetometer (microscope) and the time needed

Table I

d_{25}^{25}	Method of measurement	Year	Author
1.10775±0.00003	Mass spectrometer	1945	Kirschenbaum, Graff, Forstet 4
1.07744	Mass spectrometer	1945	Woskuil and Barash 4
1.10774±0.00001	Correction for oxygen introduced into measurements of Tronsted 5	1954	Isberg and Lundberg 6
1.10770±0.00001	Density method	1951	The present work
1.10772±0.00001	Nuclear magnetic resonance	1951 1952	The present work
1.10774±0.00002	Mass spectrometric	1952 1953	The present work

for a movement of 1 mm was noticed. In the temperature interval of ± 0.020°C above or below the temperature of flotation, the velocity of the float showed a linear relation with the departure from the true flotation temperature. The relation V/dt was specific and almost constant for each single float.

The influence of changes in barometric pressure on the flotation temperature was noticed. At pressures 740 ± 90 mm Hg, and at a temperature of 20.745°C a linear relationship with the measured density was observed. It was 0.0344 γ d/mm Hg. However, from the papers published by Fromherz, Sonderhoff and Thomas[9] a greater value of 0.0435 γ d/mm Hg was calculated. This difference is due to the different compressibility of the two floats used. The data in Table I are corrected for a pressure of 740-mm Hg and the figures rounded off to 0.1 γ d. A method of sample purification was worked out which was specific for each kind of contamination. Oxidative, acid, basic, or combined treatment was repeated until constant results were reached. The purity of samples was checked by measuring the conductivity of samples which never exceeded 2×10^{-6} ohm^{-1}.

Table II on this page gives some information about the abundance of isotopes in natural and in industrial samples of home waters in terms of density deviations. Most of the results were obtained by the temperature-float method and compared with our standard tap water of Ljubljana. In spite of great time losses, we preferred the temperature-float method to the magnetic-float method for its reliable and accurate results. It was found by repeated tests that the limit of accuracy was ± 0.2 γ density.

Table II

Samp. no.	Place of sampling	Source of water	Date of sampling	T°C	Density γd (1γd = 10^{-6} g/cm³
1	Electric works, Trbovlje	Raw water of main tank	4/2/54	−0.001	−0.2
2	Electric works, Trbovlje	Boiler (100T/h) Boiler water	4/2/54	+0.001	+0.2
3	Electric works, Velenje	Water out of pond	9/2/54	+0.001	+0.2
4	Electric works, Velenje	Water out-of-pond, dehardened (soda-lime process)	9/2/54	+0.001	+0.2
5	Electric works, Velenje	Boiler (20T/h, 400°C) Boiler water	9/2/54	+0.026	+5.4
6	Textile factory, MTT Maribor	Boiler feed water	27/1/54	−0.003	−0.6
7	Textile factory, MTT Maribor	Boiler I (13T/h) 4% boiler water	27/1/54	+0.002	+0.4
8	Textile factory, MTT Maribor	Boiler II (5T/h) 10% boiler water	27/1/54	0.000	0.0
9	Institut "J. Stefan"	Distilled water, occasional sample	15/9/53	−0.004	−0.8
10	Institut "J. Stefan"	Distilled water, I fraction 100 ml/2000 ml	5/6/53	−0.010	−2.1
11	Institut "J. Stefan"	Distilled water, last but one frac. 130 ml/2000 ml	5/6/53	+0.014	+3.0
12	Institut "J. Stefan"	Distilled water, last fraction 55 ml/2000 ml	5/6/53	+0.028	+5.9
13	Institut "J. Stefan"	Distilled water, quartz apar. residue after 40h	11/6/53	+0.005	+1.0
14	Thermal bath, Niska Banja	Thermal well	4/3/53	+0.0005	+0.1
15	Dead Sea	Sea water, we are indebted to Prof. Sambursky for sample	24/1/55	+0.011	+2.3

(Continued on next page)

Table II. (Continued)

Samp. no.	Place of sampling	Source of water	Date of sampling	T°C	Density γd (1γd = 10^{-6} g/cm³
16	Adria, bay near Koper	Sea water	12/2/55	+0.012	+2.5
17	Salt-works, Piran Sv. Lucia	Residual water after crystallisation I	9/12/54	+0.016	+3.3
18	Salt-works, Piran Sv. Lucia	Residual water after basin II	9/12/54	+0.008	+1.7
19	Salt-works, Piran Sv. Lucia	Residual water after basin III	9/12/54	+0.018	+3.8
20	Salt-works, Piran Sv. Lucia	Residual water after basin IV	9/12/54	+0.014	+2.9
21	Salt-works, Ulcinj	Residual water after basin 29	19/3/53	+0.022	+4.6
22	Inst. "J. Stefan"	Residual water from air conditioning (1 year old)	21/1/55	+0.039	+8.2
23	Elektrobosna, Jajce	Water dehardened by Wofatit	5/2/54	−0.001	−0.2
24	Elektrobosna, Jajce	Caustic soda after electrolysis	5/2/54	+0.002	+0.4
25	Saturnus Ljubljana	Water	15/2/54	+0.000	0.0
26	Saturnus Ljubljana	Nickel plating bath, 10 years old	15/2/54	+0.009	+1.9
27	Saturnus Ljubljana	Chromium plating bath, 7 years old	15/2/54	+0.012	+2.5
28	Saturnus Ljubljana	Copper cyanide bath, 2 years old	15/2/54	+0.001	+0.2
29	Saturnus Ljubljana	Silvering bath	15/2/54	+0.007	+1.5
30	Saturnus Ljubljana	Abandoned Al-oxydation bath	15/2/54	+0.006	+1.3
31	Unitas, Ljubljana	Sulfuric acid solution, fresh	17/2/54	−0.004	−0.8
32	Unitas, Ljubljana	Sulfuric acid solution, exhausted	17/2/54	+0.009	+1.9
33	Iron-works "Zelezarna Jesenice"	Water	5/2/54	−0.002	−0.4
34	Iron-works "Zelezarna Jesenice"	Sulfuric acid bath, exhausted	5/2/54	+0.010	+2.1
35	Copper-works, Bor "Bazen Bor"	Water for electrolysis	16/3/54	−0.009	−1.9
36	Copper-works, Bor "Bazen Bor"	Copper refination electrolyt	16/3/54	+0.021	+4.4
37	Brewery "Union", Ljubljana	Original water	24/11/54	−0.001	−0.2
38	Brewery "Union", Ljubljana	Malt	24/11/54	+0.011	+2.2
39	Brewery "Union", Ljubljana	Beer, water fraction	24/11/54	+0.005	+1.1
40	Brewery "Union", Ljubljana	Beer, alcohol fraction burned in oxygen	24/11/54	−0.048	−10.0
41	Brewery "Union", Ljubljana	Beer, residue after distillation, burned in oxygen	24/11/54	+0.012	+2.5
42	Brewery "Union", Ljubljana	Beer, total, burned in oxygen	24/11/54	+0.002	+0.4
43	Gasworks, Ljubljana	City, tap water	28/8/53	0.000	0.0
44	Gasworks, Ljubljana	Condensate from air cooler	28/8/53	+0.007	+1.5
45	Gasworks, Ljubljana	Condensate from water pipe cooler	28/8/53	+0.002	+0.4
46	Gasworks, Ljubljana	Water out of scrubber	28/8/53	+0.001	+0.2
47	Gasworks, Ljubljana	Gas, dry, burned in air	28/8/53	0.000	0.0
48	Elektrobosna, Jajce	Hydrogen tank I	5/2/54	−0.016	−3.4
49	Elektrobosna, Jajce	Hydrogen tank II	5/3/54	−0.035	−7.6

(Continued on next page)

Table II. *(Concluded)*

Samp. no.	*Place of sampling*	*Source of water*	*Date of sampling*	*T°C*	*Density γd (1γd = 10^{-6} g/cm³*
50	Hydrogen works, Lambach	Hydrogen tank II	30/3/54	−0.015	−3.2
51	Chem. factory, Hrastnik	Water	—	−0.002	−0.4
52	Chem. factory, Hrastnik	Residual water after soda crist.	25/2/54	0.000	6.0
53	Chem. factory, Hrastnik	Mother liquor chromium alumn.	25/2/54	−0.001	−0.2
54	Chem. factory, Hrastnik	Mother liquor iron sulfate	25/2/54	+0.002	+0.4
55	Zink works, "Cinkarna Celje"	Mother liquor copper sulfate	23/1/55	+0.010	+2.1
56	Zink works, "Cinkarna Celje"	Mother liquor chromium alumn.	23/1/55	+0.004	+0.8
57	Chem. factory, "Zorka Šabac"	Mother liquor copper sulfate	3/2/55	+0.006	+1.3

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Temperature Dependence of the Deuterium Distribution in the Reaction $LiAlH_4$ + 4 HDO

By P. Savić, N. Dogramadži, M. Novaković,* Yugoslavia

The distribution of deuterium in the reaction $LiAlH_4$ + 4 HDO at 80°, 60°, 20°, 0°C was examined and it was found that after the reaction, the concentration of deuterium was reduced to almost half the initial value. With decrease of temperature the concentration of deuterium in the gaseous phase is diminished only very slightly.

The exchange between the deuterium of heavy water and the products of reaction (LiOH and $Al(OH)_3$) was examined.

The concentration of deuterium in the solvents (dioxane and di-*n*-butyl ether) after the reaction was investigated. No exchange was observed.

The hydrogen from this reaction can be used for determination of deuterium in heavy water in the concentration range of 0.017–0.815% D_2 by means of mass spectrometer.

INTRODUCTION

$LiAlH_4$ is often used in reduction reactions in organic chemistry. In these reductions, strongly negative elements, such as O_2, N_2, Cl, Br, and I, are displaced by the hydrogen from hydride.[1,2]

As a Grignard reagent, $LiAlH_4$ can be used for the determination of mobile (active) hydrogen atoms.[3] Bake and MacNevin[4] have used $LiAlH_4$ as a reagent for the determination of water, and they have also attempted to explain the mechanism of that reaction. According to them, if there is an excess of $LiAlH_4$, the reaction would not stop at:

$$LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$$

but would continue with the reactions:

$$4Al(OH)_3 + 2LiAlH_4 \rightarrow 2LiOH + 3Al_2O_3 + H_2O + 8H_2$$

or:

$$LiOH + 2Al(OH)_3 \rightarrow LiH(AlO_2)_2 + 3H_2O$$

so that the molar ratio H_2/H_2O would be equal to 1.6 and not 1. Wendwer *et al.*[5] have made use of this reaction to produce pure HD. The purity of HD or the percentage of H_2 and D_2 depended on the temperature and the molar ratio of H_2O to $LiAlH_4$.

Since the reaction of $LiAlH_4$ with water is convenient for evolution of hydrogen we have tried to apply this method for the preparation of deuterium for analysis of the D_2 concentration in water by means of a mass spectrometer.

As the ratio of H_2 to D_2 changes with the variation of the molar ratio and temperature we have undertaken to examine the deuterium distribution at different temperatures during this reaction. We have also examined the exchange between heavy water and the solvents used (dioxane and di-*n*-butyl ether), as well as the products of the reaction: LiOH and $Al(OH)_3$ so as to obtain information regarding the mechanism of the reaction for the molar ratio of $LiAlH_4/H_2O$ equal to 1/7.5.

EXPERIMENTAL PROCEDURE

Special attention was paid to the preparation of solvents. 250 ml of dioxane or di-*n*-butyl ether were first heated under reflux with Na. When Na stopped reacting, 0.5-gm of $LiAlH_4$ were added and the contents transferred to a Claisen flask which was connected via a condenser to a vacuum system (Fig. 1). After the solvent had been frozen with liquid air and the system evacuated, purification of the solvent was continued by heating in an oil bath at 80–90°C, for 2–3 hours. The solvent was then distilled in vacuo and the whole procedure repeated until reaction with $LiAlH_4$ ceased, e.g., until in the system consisting of 250 ml of solvent and 0.5 gm of $LiAlH_4$ at 80°C, a hydrogen pressure of 8–10 cm was developed only after 2 hours. The solvent was distilled from $LiAlH_4$ and then used in the reaction. A measured amount of $LiAlH_4$ was heated with the solvent for one hour at 80–90°C, and after being frozen with liquid air it was evacuated. A given amount of water was then added. Combustion of the hydrogen took place in the CuO tube, and methane was produced from the condensed water by use of a Grignard reagent. The concentration of deuterium in the methane was measured with a mass spectrometer being a method previously described.[6]

EXPERIMENTAL RESULTS

For the rection with $LiAlH_4$, the concentrations of the water in mol % D_2 were: 0.274, 0.530, 0.815. The molar ratio of water to $LiAlH_4$ was 7.5. Since the reaction is exothermic it was difficult to maintain the temperature within very narrow limits. The

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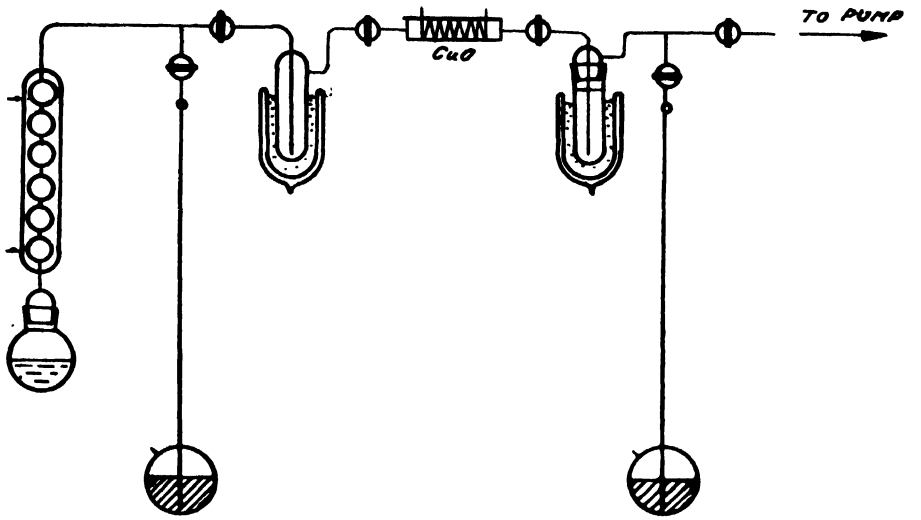

Figure 1. The equipment for the reaction of $LiAlH_4$ with water

temperature obtained after introduction of water into the ether solvent, and then maintained by slow heating, was considered as the temperature of the reaction.

Table I

Initial conc. D_2 in water	*Temp. of reaction*	*Reaction time in min*	*Conc. of D_2 in hydrogen*
0.274	0°C	30	0.114 ± 0.005
0.274	60°C	28	0.122 "
0.530	0°C	30	0.270 "
0.530	20°C	30	0.270 "
0.530	80°C	30	0.270 "
0.815	0°C	28	0.390 "
0.815	20°C	28	0.398 "

The concentrations of deuterium in the hydrogen after the reaction with $LiAlH_4$ and HDO, are given in Table I together with the temperature and the reaction time.

As LiOH and $Al(OH)_3$ are formed during the reaction, an exchange could take place between the deuterium from the heavy water and the hydrogen from hydroxyl groups. For that reason we have examined the exchange of LiOH and $Al(OH)_3$ with water enriched in deuterium. LiOH and $Al(OH)_3$ were first dried at 120°C for 6 hours and then evacuated for 1 hour. After the heavy water was introduced, the whole system was shaken at 20°C. Finally the water was distilled off under vacuum and analysed. The experimental results are given in Table II.

Table II

Compound	*Exchange time in hr*	*Molar ratio X:HDO**	*Equilibrium constant*
LiOH	0.5	1:2.4	0.6
LiOH	10	1:2.4	0.6
LiOH	0.5	1:5.5	0.5
$Al(OH)_3$	0.5	1:7	1.7
$Al(OH)_3$	10	1:7	1.7
$Al(OH)_3$	0.5	1:8	1.8

* *X* is LiOH or $Al(OH)_3$.

Table II shows that the exchange between hydrogen from the ether and deuterium from the heavy water is quite possible. The solvents dioxane and di-*n*-butyl ether were therefore, also examined. After the reaction of heavy water with $LiAlH_4$, the solvent was separated, burned over CuO in an oxygen flow. It was found that there was no exchange between the ether and the water.

DISCUSSION OF RESULTS

The influence of the temperature on the distribution of heavy water during the reaction $LiAlH_4 + 4\,HDO$ is negligibly small. Somewhat lower concentration of D_2 at 0°C is almost within the limits of error. Table I shows that all investigations have given the same results: after the reaction, the concentration of D_2 is reduced to almost half the initial value, in the given time. We conclude therefore, that the reaction between $LiAlH_4$ and heavy water in the molar ratio of 1/7.5 proceeds so that the deuterium from the water is evenly distributed between the hydrogen gas and LiOH and $Al(OH)_3$. The hydrogen from the $LiAlH_4$ which contains 0.017% of D_2 combines in the same molar ratio with the deuterium which is liberated from the heavy water during the reaction so that the concentration of the gas phase is reduced by one half. The distribution of deuterium between LiOH and $Al(OH)_3$ is determined by the equilibrium constants, which are 0.5 ± 0.1 for LiOH and 1.7 ± 0.1 for $Al(OH)_3$.

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Record of Proceedings of Session 16B.1

TUESDAY AFTERNOON, 16 AUGUST 1955

Chairman: Mr. F. Giordani (Italy)

Vice-Chairman: Mr. A. Clemente (Philippines)

Scientific Secretaries: Messrs. A. Finkelstein and B. Prakash

PROGRAMME

P/819 Survey of heavy-water production processes ..... M. Benedict

P/774 The design of isotope separation plants: some basic design equations for the distillation process ..... I. Dostrovsky and Y. Lehrer

P/927 Final concentration of heavy water by rectification .... P. Baertschi and W. Kuhn

P/958 Efficiency of some catalysts in the exchange reaction between heavy water and hydrogen ..... P. Savić *et al.*

DISCUSSION

P/410 Infra-red methods for the analysis of heavy water ..... J. Gaunt

P/631 On methods of isotopic analysis of heavy water K. W. Vladimirsky *et al.*

DISCUSSION

Mr. M. BENEDICT (USA) presented paper P/819.

Mr. I. DOSTROVSKY (Israel) presented paper P/774.

Mr. P. BAERTSCHI (Switzerland) presented paper P/927.

Mr. S. RIBNIKAR (Yugoslavia) presented paper P/958 as follows: In one of our earlier projects, in which we compared the catalytic activity of certain catalysts, usually employed in hydrogenation, on the isotope exchange reaction between heavy water and hydrogen, we found that reduced nickel tungstate was much more active than zinc chromate, maganese chromate and chromium trioxide (three catalysts used in hydrogenation). It seemed, therefore, worthwhile studying the catalytic properties of certain compounds similar to nickel tungstate.

Reduced nickel, cobalt and iron chromates, tungstates and molybdates; chromium tungstate and molybdate, reduced nickel and cobalt oxides and, for purposes of comparison, a platinum catalyst, were synthesized. All the compounds listed were obtained by precipitation from aqueous solutions. After drying, the substances were reduced in a stream of hydrogen at 400°C. Their surface areas, the amounts of hydrogen adsorbed and the average pore sizes were determined by the usual methods. The exchange reaction was carried out in an apparatus in which there is a constant flow of gas. The pure natural hydrogen passes through the "humidifying tube," where it becomes saturated with water vapour containing 0.5 per cent D_2O. The hydrogen/water mole ratio is kept at a value of about 4 by means of a suitable thermostatting device. The hydrogen/water vapour mixture passes into the catalyst tube which is held at a temperature of 110°C. After that the water is condensed and then analyzed by mass spectrometry. The reduction in the concentration of heavy water in the original sample is taken as a measure of catalytic activity. The results are shown in Slide I (Table I of P/958).

The exchange reaction on nickel catalysts is very rapid, such that the exchange time on their surfaces may be of the order of $\frac{1}{10}$th to 1 second. Chromium catalysts also show great activity, but the activity of cobalt catalysts is very much less. We were unable to observe any activity in the case of catalysts containing iron.

It can be seen from the data in Slide 2 (Table II of paper P/958) that, with one slight exception in the case of reduced cobalt chromate, the specific activity falls sharply in the order: nickel-chromium-cobalt-iron; similarly there is a visible drop in the order: tungstates-chromates-molybdates-reduced oxides.

The data on hydrogen adsorption clearly prove that total adsorption power does not play an essential part in catalytic activity; for example, the most active catalyst (nickel tungstate) adsorbs ten times less hydrogen than the inactive catalysts. The absence of exchange activity in iron catalysts may be interpreted in two ways:

1. It is well known that when iron catalysts are used in ammonia synthesis, water acts as a catalytic poison, and this may also apply to the isotope exchange reaction;

2. On the basis of the work done by Hirota and Horiuti, who found that the catalytic efficiency of metallic iron is 200 times less than that of nickel at 100°C, it may be assumed that such minute activity is outside the limits of sensitivity of our measuring

instruments. For these catalysts, however, as also for reduced cobalt oxide, the exchange time is more than one minute.

DISCUSSION OF P/819, P/774, P/927 AND P/958

Mr. R. F. D. RITCHIE (New Zealand): The production of heavy water in New Zealand is mentioned in Mr. Benedict's paper. As several delegates have expressed interest in the New Zealand activities I should like to add a few words concerning them.

Early in 1950 investigation of the natural geothermal resources to be found at Wairaki in the centre of the North Island was commenced, and since then a number of steam bores have been sunk with encouraging results. At first, these investigations were mainly directed to electricity generation, but as one of the methods of producing heavy water is by distillation and as an abundant supply of natural heat is available in this steam, the possibility of producing heavy water as a valuable by-product was later investigated in association with United Kingdom scientists.

Early this year a company called Geothermal Development Limited was formed to exploit the natural steam, and the stage has now been reached where as a contribution towards the development of nuclear power plant for industrial purposes an integrated plant to use this natural steam for the production of both electricity and heavy water is being designed in the United Kingdom in association with leading mechanical, chemical and civil engineering consultants engaged jointly by the company. It is proposed that the initial integrated plant to be constructed for the company will have an installed capacity of about 40,000 kw, but provision is being made for extension as additional steam becomes available from further boring.

Mr. E. ROTH (France): I have two questions for Mr. Benedict: First, does he feel that a method of exchange between hydrogen and ammonia alone would be a practicable substitute in ammonia plants where it might not seem an economic proposition to install hydrogen distillation apparatus? Second, could the method mentioned, of exchange between hydrogen, ammonia and water compare economically with that of exchange between hydrogen sulphide and steam?

Mr. BENEDICT (USA): The first question, if I understood it right, was whether it would be desirable under certain circumstances to use the exchange reaction between hydrogen and ammonia to recover deuterium at an ammonia plant instead of the distillation of hydrogen. I myself have not made any studies on this process, and I really am not in position to give an assured answer. I would point out, however, that all these exchange processes have the characteristic of not being able to recover 100 per cent of the deuterium present in hydrogen feed, and for that reason I think this might be one disadvantage of this process.

The other question, as I understood it, had to do with the possibility of using a dual-temperature hydrogen-ammonia exchange reaction coupled with an exchange reaction between steam and ammonia in order to bring deuterium into the plant, a process which was mentioned briefly in the written presentation. Again, not having made detailed engineering studies, I cannot give an assured answer but it is my feeling that the necessity for providing the additional exchange step between steam and ammonia, together with the fact that one would need to use a catalyst for the ammonia-hydrogen exchange portion of the process, which according to present knowledge would consist of something like a potassium amide dissolved in liquid ammonia which would have to be recovered quite completely from the ammonia leaving the dual-temperature portion of the plant, would so complicate the process and add to the cost as to make the process probably less attractive than the other exchange process I mentioned. I would not want this to be considered as a really informed opinion; it is something one would have to study.

Mr. E. ROMETSCH (Switzerland): Is it possible to give the ratio of capital costs and operating costs in the initial heavy-water price of $28 per pound?

Mr. BENEDICT (USA): I am sorry to say that I cannot give full information in answer to that question. All I can say is that the $28 per pound as the price of heavy water is the price which was arrived at by the accountants of the United States Atomic Energy Commission taking into account the whole information on what it has cost to build and operate the Atomic Energy Commission's plants, using conventional government accounting procedures, and was set up so that there would be neither loss nor profit to the United States government in selling heavy water at that price.

Mr. DOSTROVSKY (Israel): Could you say something of the way in which you overcame the corrosion difficulty of H_2S?

Mr. BENEDICT (USA): I am afraid that is a question I am just not prepared to answer.

Mr. ROTH (France): Can Mr. Ribnikar tell us whether he measured the amounts of water absorbed on the various catalysts and whether the activity observed depended on those amounts?

According to measurements which we have made ourselves, the exchange times observed in the case of platinum were of the order of a hundredth rather than a tenth of a second. It is possible that this discrepancy is due to using different proportions.

Mr. RIBNIKAR (Yugoslavia): We have not measured the amounts of water absorbed in these catalysts, but if the exchange is repeated several times over a catalyst, the catalyst's activity does not vary by more than about thirty per cent.

Mr. BENEDICT (USA): I would like to inquire whether it would be possible to have, in addition to the data given in your paper, information on the

amount of catalyst used in each run, and the flow rate of gas so that it would be possible to work up information in a different manner than is presented. Do you think you could supply us with that information?

I also wanted to inquire whether you had done any work or had any opinion on the activity of promoted catalysts or catalysts containing mixed elements instead of the pure compounds which you studied.

Mr. RIBNIKAR (Yugoslavia): I did not quite understand the term "mixed catalysts," as all these catalysts are combinations of two different elements.

Mr. BENEDICT (USA): The first question was whether it would be possible to obtain additional information on the quantity of the catalyst.

Mr. RIBNIKAR (Yugoslavia): In these experiments there is about a tenth of a gram to a gram of catalyst with a gram or a little more of water, and a hydrogen flux of about four or five litres per hour.

Mr. BENEDICT (USA): I have a question to the authors of paper P/927. I was very intrigued by the account of their very neat and efficient pilot plant and wondered whether they could supply some additional information to give some notion of the size of the equipment involved. In the case of the pilot plant the flow sheet of which was given, can they tell me the diameter of the individual tubes and how many tubes were used in parallel to do the job?

Mr. BAERTSCHI (Switzerland): for the first stage we used about 100 tubes of 20 mm diameter. The second stage was just one tube. We used wire gauze packing or multi-turn helices.

Mr. R. LILJEBLAD (Sweden): What does Mr. Benedict consider the economic concentration of heavy water with hydrogen sulphide and water? I suppose it will not be economic to go to 99.8% and one would use the distillation method for the last concentration, but can you tell us to what concentration you think it practical to go?

Secondly, in your calculations how have you generally figured the capital costs?

Mr. BENEDICT (USA): In reply to the first question, the answer would depend a good deal on the scale of production in the individual plant. One might say that one would like to change over from the hydrogen sulfide process to some other process as soon as the concentration was high enough, so that the next step could be done in a single piece of equipment. For example, if one could use one of these distillation plants without having to have several of them in parallel, that would be a good time to change over. The larger the scale of operation, the higher the concentration you would have. I do not carry the figures in my head.

The 5% figure was intended to represent all the charges against plant investment, interest at a low rate as well as plant depreciation, and was simply illustrative of what we find when we talk about long-life government-financed plant.

Mr. J. GAUNT (UK) presented paper P/410.

Mr. K. V. VLADIMIRSKY (USSR) presented paper P/631 as follows: Many methods have been proposed for determining the isotopic composition of a mixture of heavy and ordinary water. The most frequently encountered are those based on density measurement—the pyknometric, drop and float methods. These methods do not require complicated apparatus and highly-trained staff and they yield a high degree of accuracy. The disadvantage of the density methods is the possibility of systematic error due to inaccurate determination of the constant on which calibration is based, namely, the density of isotopically pure deuterium oxide. The object of this research has been to determine this constant precisely. In addition to direct measurements of the density of the substance at its maximum concentration, parallel measurements were made of its density and isotopic composition.

1. To obtain heavy water containing a maximum concentration of deuterium, two identical rectification columns were built of stainless steel with a liner of perforated nickel. Heavy water obtained by electrolysis was poured into one of the columns and heavy water produced by distillation into the other. For the duration of each operating cycle, which lasted 120 hours, the columns worked without sampling; at the end of the cycle the water from the collector, enriched with the light isotope, was drained off, and the separation process continued with a lower starting concentration of the light isotope.

The densities were measured by the differential pyknometric method. The isotopic composition of the oxygen was standardized by means of the isotope-exchange reaction with dried, natural carbon dioxide. Moscow tap-water was used as control water. The results of the density determinations of the last cycles agree within the limits of measurement error. In working on the data yielded by the measurements, the calculation of the isotopic concentrations in these experiments was based on a study of the separation process. In the first cycles the separation of hydrogen isotopes was observed directly by the increase in the density of water with a standardized oxygen isotopic composition. In the last cycles the increase in the density of the water due to the separation of oxygen isotopes was measured. An analysis of these data indicates that errors arising out of non-completion of the enrichment process do not exceed the order of magnitude of other errors which are possible in this method.

2. Of the methods of isotopic analysis which do not depend on density measurements, we have employed the nuclear magnetic resonance method and the mass-spectrometric method. The nuclear magnetic resonance method is based on the difference in the magnetic moments of the nuclei of hydrogen and deuterium, which makes it possible to measure the resonance amplitudes of both isotopes without mutual

interference and ensures that no systematic error can occur at maximum concentrations, in particular at a deuterium concentration near 100%.

The apparatus designed for these measurements must give very stable readings, especially when samples are changed. For that reason we used instruments without high-frequency compensation. To improve the signal/noise ratio, we used narrow-band systems of two kinds—the synchronous filter and the ordinary synchronous detector.

The accuracy of the measurements is determined mainly by the amount of noise and by the consistency of amplification of the recording instrument. A further possible source of error is interference due to signals from various parts of the sample resulting from a lack of homogeneity in the magnetic field. To reduce the influence of this effect, the measurements were taken on water samples containing paramagnetic salts in solution, which increased the natural width of the resonance line.

The use of paramagnetic salts also substantially simplifies the dependence of signal amplitude on the isotopic concentrations being measured. In the case of pure water, this dependence may be non-linear, since apart from the number of nuclei of a given isotope in the sample the dependence of the relaxation times on the isotopic composition may be considerable. In solutions of paramagnetic salts, the fundamental mechanism restoring thermal equilibrium is the interaction of the magnetic moments of the nuclei with the moments of the paramagnetic ions, and this does not depend on isotopic concentrations. In this case, the signal amplitude is strictly proportional to the concentration.

Solutions of paramagnetic salts in heavy water were prepared for the measurements with varying deuterium concentrations, including two solutions in highly concentrated heavy water. Samples of a volume of 4 cm^3 of the original solutions were prepared for the measurement of the signal amplitudes of the nuclear magnetic resonance. After that, the solutions were subjected to a standard purification process and their density was measured. The density of the isotopically pure heavy water was determined by linear extrapolation to zero hydrogen concentration.

3. For the mass spectrometer measurements, an apparatus was built which would make it possible to measure the ratio of the ion currents due to D_2^+ and HD^+ ions in conditions of extremely high enrichment. The vacuum system was subjected to a long heating and washing process by means of gas containing 99.75% deuterium. The ion source was so constructed that corrections could be determined experimentally by the two-filament method, for the discrimination effects due to the incandescent filament. The corrections for the resolving power of the instrument and for D_3^+ and D^+ ion formation were also determined experimentally. Gas samples for analysis were prepared by isotope exchange between the original water sample and gaseous deuterium. Platinum black was used as the catalyst.

Density and isotope-concentration measurements were performed for four different deuterium concentrations. Samples for the determination of isotopic composition were taken directly from the pyknometer after their density had been ascertained. Just as in the case of the nuclear magnetic resonance method, the density of isotopically-pure heavy water was determined by linear extrapolation to zero concentration of the light isotope.

The results of our measurements, obtained by the three different methods, are tabulated in the paper (P/631) and compared with the measurements of other authors. The results obtained by the nuclear magnetic resonance method and the mass-spectrometry method agree, within the limits of experimental error, between themselves and with the most reliable measurements by other authors. The results of density measurements for the most highly concentrated product are lower by 0.002–0.004%. The values obtained by the nuclear magnetic resonance method, with some increase in the indicated error, may be taken as the average result of all our measurements. The main source of systematic error is dilution by natural water. The possible systematic errors in the nuclear magnetic resonance method and the mass-spectrographic method are bound to have different signs, which substantially increases the reliability of the results obtained.

In the method employing nuclear magnetic resonance, the sources of systematic error can be substantially reduced by taking the density and hydrogen concentration measurements on the same samples, using a pyknometer filled with a specimen of heavy water as a sample for measuring by the nuclear magnetic resonance method. The nuclear magnetic resonance method is clearly the most reliable for taking absolute measurements for calibration purposes. The best method for analysis is undoubtedly the method just described by Mr. Gaunt.

DISCUSSION OF P/410 AND P/631

Mr. E. Roth (France): The two papers which have just been presented indicate that, in the aqueous phase at least, there are no longer any serious problems involved in measuring the isotopic concentration of the water. We are ourselves using the very elegant techniques described by Mr. Gaunt, as well as mass-spectrometry techniques.

I would, however, like to mention that, in our view, methods based on measurement of thermal conductivity may, in the gaseous phase, be a good substitute for mass-spectrometry methods, especially if used to observe catalytic reactions such as those mentioned by Mr. Ribnikar.

I would like to ask Mr. Vladimirsky whether he could give us details about the two-filament ion source. Are the two filaments lit simultaneously, as in the de Haye source, and what is their purpose?

Mr. VLADIMIRSKY (USSR): The two-filament method to which I referred is as follows: As is well-known, there is much difficulty in using the mass spectrometer when the difference between the concentrations of the isotopes which are being measured is large; this difficulty is due to the fact that the electron flux in the ion source alters the isotopic composition of the gas, on account of the molecules absorbed by the instrument walls. In the two-filament method, two electron-flux sources are used, *i.e.*, two cathodes. Three experiments are performed with the cathodes switched on separately and simultaneously. The ratio of the isotope concentrations is determined by assuming that the catalytic action of the electron fluxes is additive. Experiments in which the instrument is primed over a long period have shown that this procedure increases the accuracy of the measurements considerably.

Mr. C. J. RODDEN (USA): This is a question to Mr. Vladimirsky: In the light of the present paper, what is the most precise way of determining heavy water?

Mr. VLADIMIRSKY (USSR): I think that of the possible methods the density method is the most accurate. The method developed by Mr. Gaunt is very good in that it combines accuracy with rapid performance of the analysis. It takes about twelve hours to perform a precise analysis by the density method.

Mr. RODDEN (USA): Do you have memory effects in your mass spectrometer?

Mr. VLADIMIRSKY (USSR): Yes. It was precisely for that reason that the instrument was primed for such a long period with a hydrogen concentration very similar to the concentration on which the actual measurements were taken.

Mr. RODDEN (USA): Mr. Gaunt, what is used for the cell windows, and is corrosion of the windows a problem?

Mr. GAUNT (UK): Corrosion of the windows is not a problem. In the high concentration range, measurements are made at 3 microns and here the windows can be of calcium fluoride, synthetic sapphire or best of all, fused silica. For the 50% range the measurements are made at 1.4 microns and glass windows can be used. For the 0–3% region, where the measurements are carried out at 3.98 microns, calcium fluoride gives the best results although synthetic sapphire can be used.

None of these materials is affected by water.

Session 16B.2

PRODUCTION TECHNOLOGY OF SPECIAL MATERIALS: GRAPHITE

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The Production and Properties of Graphite for Reactors

By L. M. Currie, V. C. Hamister, and H. G. MacPherson,* USA

Graphite was used for the first reactors because it was the most readily available material that had reasonably good moderating properties and a low neutron capture cross section. Other desirable properties that made its use widespread even in low-temperature reactors were its low cost and ease of precise machining. More recently, great interest has been shown in the superior properties of graphite as a high-temperature refractory and as a container for liquid metals. For future reactors, graphite will be given most serious consideration as a construction material where high temperature operation is required, or where economy of construction and of neutrons is desired in combination with the generation of commercial power.

The neutron economy arises from the fact that pure graphite has a neutron capture cross section[1] of only $0.0032 \pm 0.0002 \times 10^{-24}$ cm^2. Commercial purified graphite has been produced in quantity with a cross section of 0.0037×10^{-24} cm^2. Taking into consideration the atomic density of normal reactor graphite (bulk density 1.67 gm/cm^3), the bulk neutron absorption coefficient is 0.00031 cm^{-1}. Taking the inverse of this figure we get the physical picture that a slow neutron may travel a total distance of about 32 meters in graphite without capture.

The moderating ability of graphite arises, of course, from its relatively low atomic weight. Considering the relative masses of the neutron and carbon nuclei, a fast neutron will lose on the average 0.158 of its energy at each collision. With a carbon scattering cross section of 4.7×10^{-24} cm^2, a neutron will travel on the average 2.53 cm in reactor graphite of density 1.67 gm/cm^3 between collisions with carbon atoms. Combining these figures yields a slowing-down power of 0.0625, indicating that, on the average, a fast neutron will lose 6.25 per cent of its energy per cm travel through bulk graphite.

The ratio of the slowing-down power to the bulk absorption coefficient has been called the moderating ratio,[2] and is used as a rough figure of merit for a moderator material. This figure for graphite is 202, which compares favorably with all other common moderator materials except heavy water. The following table gives a comparison of the moderating qualities of graphite with a few other materials.[2]

Graphite is unique in its position among materials of construction, resembling both metals and ceramics in some of its properties. It has high thermal conductivity, conducts electricity, and is black when finely divided and in these respects resembles a metal. On the other hand, it lacks ductility and is porous and in these respects behaves like some ceramics. Furthermore, its manufacture resembles that of ceramics rather than metals, since it cannot be melted and cast, rolled, forged, or welded. It differs from most ceramics in that it is easily machined—more so even than any metal. Its low thermal expansion in combination with its high thermal conductivity and strength at high temperatures makes it the most resistant to thermal shock of any material.

The most important limitations of graphite are that it oxidizes at high temperatures when exposed to air, and is permeable to gases and liquids. Research is continuing with respect to both of these problems and it is reasonable to expect considerable progress in the near future. Pipe is already available that is impervious at moderate pressures, and further progress in this direction is expected to result in the development of a suitable reactor graphite that will contain liquid metals. It is reasonable to expect also the development of coatings for such graphite that will resist oxidation over limited temperature ranges.

PRODUCTION OF REACTOR GRAPHITE

Artificial graphite can be manufactured from almost any organic material that leaves a high-carbon residue on heating. Petroleum coke is the best of the available raw materials, however, and all of the graphite used in the United States for reactor moderators has been made from petroleum coke. The manufacturing process for reactor graphite will first be described, and after that the variations in properties that can result from different raw materials or processing methods will be indicated.

The petroleum coke is prepared in refineries by the polymerization and distillation of volatiles from a heavy refinery oil. The polymerization temperature used is approximately 450°C. The raw coke, as obtained from the refinery, is still a hydrocarbon with only about 95% carbon and on heating gives off a considerable amount of hydrocarbon gas. Table II summarizes the results of a great many analyses on petroleum cokes from a large variety of sources:

The coke, as received from the refinery, is fired or calcined to a temperature of about 1300°C. This is usually accomplished in a large rotary gas- or oil-fired kiln. The volatiles of the coke are burned

* National Carbon Company

Table I. Comparative Moderating Qualities

	Slowing down power (cm^{-1})	*Moderating ratio*
Graphite	0.0625	202
Beryllium	0.16	145
Beryllium oxide	0.11	183
Water	1.36	62
Heavy water	0.18	5000

Table II. Analysis of Raw Petroleum Coke

	Usual range	*Typical value*
% volatile matter at 1000°C	7 to 16	11
% ash	0.1 to 2.2	0.7
% sulfur	0.1 to 4.3	1.5

in the kiln and contribute a great deal to the heating of the coke. This calcination step is undertaken to preshrink the coke so that volume changes on subsequent processing will be controllable, allowing the manufacture of large blocks.

Since this calcined coke is the principal raw material for the graphite, its purity is important for reactor use. Table III gives an abbreviated resume of the analyses of a number of cokes actually used for graphite manufacture. In addition to the metallic impurities indicated in the table, the calcined coke retains the major portion of the sulfur indicated in Table II. For reactor graphite, cokes are selected that have reasonably low values for the impurities boron, vanadium and titanium, although this selection is less important with modern purification methods.

Table III. Metallic Impurities in Calcined Petroleum Coke

	Usual range	*Typical value*
Total ash, % of coke	0.1 to 2.0	0.70
Parts per million impurities in coke:		
Silicon	50 to 1300	300
Iron	270 to 2000	500
Vanadium	5 to 270	70
Titanium	2 to 55	10
Aluminum	15 to 340	150
Manganese	None to 180	20
Nickel	None to 85	40
Calcium	130 to 5200	260
Magnesium	10 to 230	50
Boron	0.2 to 0.9	0.4

The calcined coke is crushed and screened to yield various sizes of "particles", ranging in diameter from 0.4 mm to 13 mm. The fines from the screening operation and any excess particles are milled to a flour, which consists of grains of coke with a continuous distribution of diameter from 2 microns up to about 300 microns. The "particles" used in forming pile-grade graphite are in the range 0.4 to 0.8-mm diameter, and these are mixed with a flour in about a one-to-three ratio to form a "blend". Figure 1 gives a typical grain-size distribution for a flour and particle blend used in the preparation of reactor-grade graphite. The points shown on the curve above 74 microns were determined by the usual Tyler screen analysis. The proportioning of smaller grains was determined by a sedimentation technique modified from the method used by Cummings.[3] Knowledge of the grain-size distribution is important since it does not change appreciably in processing.

The individual grains of coke that make up the blend are irregular in shape and have a rough surface characteristic of crushed particles. The following Table IV gives a comparison of the hydrodynamic surface area of coke particles in comparison with that calculated for spheres of the same diameter. The hydrodynamic surface areas were calculated from water permeability measurements using Carman's[4] method.

Table IV. Surface Area of Sized Particles cm^2/cm^3 of Real volume

Tyler screen sieve limits of size fraction	*Nominal diameter (microns)*	*Area of coke particles*	*Calculated area for spheres*
35/48	351	415	171
48/65	175	620	242
65/100	87.5	862	343

From the table, it is apparent that the superficial area of the irregular coke particles is about 2½ times that of spheres of the same diameter. (This surface area is not to be confused with total surface area, which includes the area of internal pores.)

The shapes of the coke particles are longer and more splintery than crushed particles of a completely isotropic material. This results from the fact that in the coking process, the aromatic molecules tend to be oriented with the planes of the benzene rings parallel to the cellular walls of the coke. These walls usually fracture so that the length of coke particles is in the direction of the layer planes of the ultimate graphite structure. Cokes from different sources fracture in different ways, some yielding longer and more splintery grains than others. Each coke source tends, therefore, to have a different particle eccentricity. This is illustrated by the following Table V, which gives the results of measurements of the dimensions of coke particles made in three mutually perpendicular directions. Each figure is the average of measurements on fifty particles, made with a special measuring microscope.

It can be seen that the two cokes have a consistently different particle eccentricity. This particle eccentricity is a very important property of the coke in determining the anisotropy of the properties of the final graphite, and it even affects the manner in which its properties change under nuclear bombardment.

The next step in the manufacture of graphite is mixing the coke blend with a pitch binder. The pitch used is a residue of coal tar distillation and has the ultimate composition shown in Table VI.

The results of measurements normally made on a pitch to determine its suitability as a cinder are given in Table VII.

Table V. Microscope Measurements of Size of Grains In Microns

Sieve size limits	*Coke source*	*Length*	*Width*	*Thickness*	*Nominal fraction diameter*	*Screen Limits*
35/48	A	580	422	315	351	294–416
35/48	B	628	465	282		
65/100	A	302	220	131	175	147–208
65/100	B	365	224	121		
150/200	A	164	105	67	87.5	74–104
150/200	B	181	102	65		

The benzol and quinoline insoluble values are taken as an indication of the distribution of molecular sizes in the pitch, with higher insoluble values indicating greater proportions of large molecules. The importance of their control is largely to insure a constancy of product.

The "coking value" of the pitch is the proportion of the pitch that is left as binder carbon after heating to 1000°C. The amount of this carbon residue varies with the rate of heating and the environment during the test. The 65% figure shown is that actually obtained in commercial practice, and can be duplicated in the laboratory by mixing the pitch with carbon flour and heating the mixture slowly.

The density and coking value of the pitch are very important properties, for high values of these will be reflected directly in a high density of graphite product.

The melting point of 100°C is determined by the "cube in air"[5] method and is a rough indication of the temperature required in extrusion. The viscosity of pitches changes rapidly with temperature. For example, a typical binder pitch showed a viscosity of 13,000 centipoise at 130°C, 2200 centipoise at 150°C and 540 centipoise at 170°C.

The mixing of the pitch with the coke blend is carried out at approximately 165°C and at this temperature the pitch is quite fluid. The proportion of pitch to coke is not an exactly fixed quantity, since the amount of pitch must be adjusted until the mixture is plastic enough to be extrudable. Pitch levels are usually in the range of 30 parts of pitch per 100 parts of coke blend. A petroleum oil is sometimes added as a lubricant for extrusion. The usual oil level is about 10% of the pitch level.

Table VI. Ultimate Composition of Coal Tar Pitches Used In Graphite Manufacture

	Range for analysis of a variety of pitches, %
Carbon	91.3–92.9
Hydrogen	4.47–4.80
Nitrogen	0.81–1.07
Sulfur	0.42–0.53
Ash	0.03–0.10
Oxygen (by difference)	1.16–2.28

Table VII

Melting point	100°C
Benzol insoluble	30%
Quinoline insoluble	9 to 16%
Density at 25°C	1.31 gm/cm^3
Coking value	65%

Either molding or extrusion techniques can be used to form the plastic mixture into the desired shapes, although extrusion is more usual. A typical extrusion press for forming bars 4½ in. × 4½ in. in cross sections will have a mix cylinder 22 in. in diameter, with 2000 lb/in^2 pressure available for compacting and extruding the mix.

In the extrusion process, the coke particles tend to line up with their longest dimension parallel to the direction of extrusion. This gives a grained structure to the final graphite, the grain running parallel to the axis of extrusion. The graphite is usually stronger in the direction of the grain and has higher thermal and electrical conductivities in this direction.

When molding is used as a forming method, the particles tend to line up with their longest dimension perpendicular to the molding force and their thinnest dimension parallel to the molding force. In this case, the minimum strength, electrical and thermal conductivities of the resulting graphite are in the direction of application of molding force. In fact, a simple way to characterize the method of forming is to measure the electrical conductivity in three mutually perpendicular directions, one of which is also perpendicular to an exterior surface of the formed graphite. Two of the three conductivities will be nearly equal, the third appreciably different. If the odd conductivity is higher than the other two, the material was extruded; if lower, the piece was formed by molding.

After forming, the "green" bars are cooled, either by laying out on steel tables or by immersion in a tank of water to harden the pitch binder and render the bars less plastic for handling purposes. These cooled, green bars may then be stored, awaiting firing, without distortion.

The first firing is done in a gas-fired furnace to a minimum temperature of about 750°C. In this first firing, the green bars must be packed tightly in granular coke or a coke-sand mixture so that the bars will not distort or slump as they are heated through the temperature range in which the pitch is liquid. The pitch binder evolves hydrocarbon gases in large quantities in the temperature range of 300°C to 500°C, and becomes rigid at a temperature of about 450°C. Above this temperature, a fairly large shrinkage takes place as the binder hardens, and it is advantageous to carry the gas-firing temperature to a minimum of 750°C to insure

easy processing in the subsequent graphitizing step. The requirement for tight packing of the bars to prevent distortion and the evolution of hydrocarbon gases limits the freedom of selection of firing furnaces. Usually large bulk-packed furnaces are used in which the firing cycle may be as long as six weeks.

After the gas firing, the carbon bars could be graphitized directly to give a graphite with a density of about 1.55 gm/cm^3. However, for reactor use (and incidentally for many other uses) a pitch impregnation step is interposed to increase the density. The gas-fired bars are pre-heated to about 250°C, placed in an autoclave and evacuated to a pressure of less than one-tenth of an atmosphere. Hot pitch is then pumped into the autoclave completely immersing the bars. A pressure of 100 psi is applied for a period of several hours to insure impregnation to the center of the bars. The cycle is completed by releasing the pressure, pumping out the unused pitch, and letting the bars drain free of as much pitch as possible.

To make graphite where extremely high purity is not required, the pitch-impregnated bars are fired directly in an electric furnace of the type invented by Acheson[6] in 1895. The basic structure of the furnace consists of a bed of fire-brick tiles laid on concrete piers, with a concrete head at each end of the furnace through which graphite electrodes are cemented as current leads. The impregnated carbon bars are placed cross-wise of the furnace, one on top of the other to form stacks of carbon. Granular coke is placed between successive stacks and enough stacks are loaded to fill the length of the furnace. The whole pack is surrounded—top, sides and bottom—with a mixture of fine carborundum, coke and sand for thermal insulation. The side insulation is held in place by removable concrete blocks. The granular coke between the stacks forms the resistor element of this high-temperature resistance furnace. Power is supplied at rates of 600 to 400 kw depending on the size of the furnace, the type of graphitizing charge and the stage of the heating cycle. A total energy of from 1.6 to 3.0 kw hours per pound of finished graphite is used, again depending on the type of furnace and the type of graphite desired. The heating cycle lasts from three to four days, and cooling the charge requires about two weeks before the graphite is cool enough to be exposed to air. The peak temperature reached ranges from 2600°C to 3000°C.

In the graphitization process, the physical properties of the carbon change markedly, as will be noted more extensively below, and many of the ash constituents are vaporized improving the purity remarkably. Table VIII shows the chemical analysis of the most important neutron-consuming elements in some commercial graphites made with carefully selected coke and using a high-graphitizing temperature. In addition, there seem to be elements such as rare earths that cannot be analyzed chemically, but which contribute appreciably to neutron absorption.

For highest purity uses, the graphite can be given a high temperature, gas-extraction process, originated by the United Carbon Products Company. The process can be applied either to graphite bars, or it can be used as a combined graphitization-purification step. For the latter, the pitch-impregnated, gas-fired bars are put through another gas-firing cycle to carbonize the pitch and reduce the volatile hydrocarbon evaporation.

Briefly, the purification process consists of bathing the bars in a purifying gas containing chlorine and fluorine while the bars are heated electrically to approximately 2500°C. The reduction of neutron absorption cross sections accomplished by this purification is so great that it indicates the removal of neutron absorbing elements (such as rare earths) that do not show up in the chemical analyses. In general, the total ash content of purified graphite is under 20 parts per million.

Finished reactor graphite, manufactured with the materials, grain size distribution, forming and firing conditions described above, has principal physical properties as given in Table IX.

EFFECTS OF RAW MATERIAL AND PROCESSING VARIATIONS

Different Petroleum Coke Sources

Table IX provides ample evidence of the variation in physical properties that can be obtained from different coke sources, using exactly the same processing method. The differences arise principally from the crude oil and the processing cycles used in the refinery prior to coking, although variations in coking procedures are also significant. Thus, one cannot count on a continuation of the same coke properties from the same refinery, since crude sources and refinery practices change over the years.

The different properties obtained from different coke sources are believed to be related to two basic factors. One is the particle eccentricity that each coke exhibits on crushing and milling, which affects the degree of alignment on extrusion. This is illustrated in Table IX by the ratio of the properties when measured parallel and perpendicular to the grain, which varies markedly between the cokes

Table VIII. Typical Chemical Analysis[7]

Coke source	% Ash	Parts per million in graphite				
		Boron	Vanadium	Titanium	Iron	Calcium
C	0.084	0.5–0.8	160	12	12	260
D	0.048	0.5–0.7	27	20	11	180
B	0.037	0.4–0.5	8	12	18	150
E	0.078	–	19	5	67	230

Table IX. Physical Properties of Reactor Graphite[8] Measured at Room Temperature

Property and units	Coke source	Property measured: Parallel to grain	Property measured: Perpendicular to grain
Specific resistance (milliohm/cm)	C	0.84	1.17
	D	0.75	1.17
	E	0.88	1.20
	B	0.57	1.20
Thermal conductivity (Cal/cm-°C-sec)	C	0.40	0.30
	D	0.44	0.32
	B	0.56	0.29
Thermal expansion (per °C × 10^{-7} at 60°C)	C	24	38
	D	15	36
	E	16	32
	B	11	27
Young's Modulus of elasticity (lb/in^2)	C	1.43	0.95
	D	1.49	0.88
	E	1.54	1.07
	B	1.99	0.79
Flexural strength	E	2120	2125
Tensile strength	E	1440	1300
Crushing strength (lb/in^2)	E	5950	6420

listed. The other principal factor of difference among petroleum cokes is the graphiticity, or perfection achieved by the graphite crystals after heating to 3000°C. A high degree of graphiticity is reflected in the table by low values of such properties as resistance and thermal expansion, and a high value of thermal conductivity.

Other Raw Materials

The following raw materials find use in the manufacture of the many types of carbon provided for industry: lampblack, gas black, charcoal, retort carbon, bituminous coal, anthracite, cokes from coal, pitch coke, petroleum coke and natural graphite.

Charcoal was used by Sir Humphrey Davey to make the electrodes he employed in the first carbon arc, but it is used today only in small quantities in "Air Cell" electrodes and activated carbons, and in some brushes.

Retort carbon was used in Europe for the electrodes for some of the early open arc lamps. It has been used by United States manufacturers in several brush grades. With the passing of the old retorts for gas making and their replacement with by-product coke ovens, retort carbon of a desirable quality has practically disappeared, and today very little is used.

Lampblack has been utilized in arc lamp electrodes of all kinds since the introduction of the enclosed arc lamp in the 1890's, and is used today in several types of carbon for the motion picture industry, in searchlights, and in brushes for various types of electric motors and generators.

Of the gas blacks, only furnace black is used to any extent and then only as an admixture to other raw materials. As an admixture to coke, it improves the density and hardness of some specialty stocks.

Bituminous coal was used in very small amounts in some of the first successful large electrodes made in the United States. It has very little commercial use today in the carbon industry.

Anthracite is used in considerable quantities in large carbon electrodes for steel and ferroalloy furnaces and in very small amounts in granular carbon for telephone transmitters.

Cokes from coal (commonly called metallurgical cokes) have been used for blast-furnace linings, but the principal use in the carbon industry in this country is as a resistor and insulating material in the graphitizing furnace.

Pitch cokes (made by coking the coal tar which results from the coking of coal in by-product coke ovens) were used for a few years for the regular production of battery electrodes, open arc carbons, brushes and small electrodes where low vanadium content was necessary, but they are not employed for these purposes today. Large amounts of pitch coke have been used in Germany for large electrodes when petroleum coke was too costly or not available. Pitch coke is also used for some electrolytic anodes where low vanadium is again an important factor.

Natural graphite is widely distributed in nature in the form of flakes, lumps, or needles, or in the cryptocrystalline masses known commercially as "amorphous graphite". Carbon manufacturers use natural graphite in the flake form in some carbon brush compositions and amorphous graphite is commonly used as an ingredient in the manufacture of seal rings.

Petroleum coke has always been the main reliance of the carbon industry for its raw material, and without this by-product of petroleum refining, the growth of the carbon and graphite industry to its present position would, to say the least, have been difficult. This material is the purest form of carbon available in sufficient quantity at cost low enough to support a carbon industry.

A natural way of comparing and characterizing the different basic raw materials is to observe the degree to which they are crystallized by heat treatment. The best measurement of crystallization is provided, of course, by X-ray diffraction methods. A more convenient approximate method, and one that yields a single figure for comparison, is the measurement of "real density" after a 3000°C heat treatment. The "real density" is defined as the density of finely ground material as measured after evacuation and immersion in kerosene. The more closely the real density approaches that for purified natural graphite, 2.26 gm/cm^3, the more graphitic is the material. Table X gives real densities measured for a variety of raw materials.

The characterization of the various raw materials given in Table X can be used to indicate several factors with respect to reactor graphite made from them. First, the bulk density that can be achieved in the final graphite will be in rough proportion to the real densities listed. For example, if by a given

Table X. Real Density at 30°C In Kerosene after Heating To 3000°C (Coltman and Glass)[9]

Activated carbon	1.46
Sugar carbon	1.50–1.58
Coconut shell char	1.51
Soft wood charcoal	1.60
Cellulose carbon	1.68
Pitch coke from wood	1.70
Hardwood charcoal	1.87
Bone char carbon	1.94
Blood charcoal	2.01
Acetylene black	2.04
Bituminous coal	2.07
Anthracite coal	2.09
Coal tar oil black	2.09
Semi-bituminous coal	2.11
Pitch coke from coal tar	2.14
Lignite	2.18
Furnace black	2.18
Retort carbon	2.23
Petroleum cokes	2.20–2.26
Natural graphite	2.26

process, a density of 1.65 is obtained for a graphite made with petroleum coke, a density of only 1.53 would be expected by the same process for a graphite made with bituminous coal. Second, the graphite crystallites are imperfect in proportion to the departure from the 2.26 density, and the greater this departure the lower the electrical and thermal conductivities of the product.

The raw materials other than petroleum coke of greatest interest for reactor use are lampblack, furnace black, and natural graphite. Lampblack has been used to prepare "graphite" for experimental nuclear work. It was used as an example of a material that is nearly isotropic in physical properties and is rather poorly crystalline. Properties of a molded graphitized lampblack stock are given in Table XI below, in comparison with a similarly molded petroleum coke stock.

The difference in density shown in the table is not very significant, because it only reflects different binder contents. The higher relativity of the lampblack stock results from its poorer crystallinity and the difference in anisotropy is apparent in the relative values of the properties in the two directions.

Table XI. Properties of Molded Graphitized Lampblack Base Stock as Compared To Molded Graphitized Petroleum Coke Stock

	Graphitized lampblack		*Graphitized petroleum coke*	
	Parallel to grain	*Perpendicular to grain*	*Parallel to grain*	*Perpendicular to grain*
Bulk density gm/cm³	1.67	1.67	1.65	1.65
Specific resistance milliohm/cm	4.6	5.1	0.99	1.45
Coefficient of thermal expansion, per °C × 10^{-7} at 60°C	41	42	27	45
Elastic modulus 10^6 lb/in²	1.25	1.06	1.16	0.69
Flexural strength lb/in²	3540	2740	4060	2490

Furnace black is of potential importance in reactor graphite because it is capable of increasing the density of petroleum coke blends. The particles of this furnace black are spherical in shape, as shown by electron microscope studies, and are approximately 0.3 micron in diameter. Since the petroleum coke flour has few grains less than 2 microns in diameter, the black is able to fill void spaces between the coke grains and, thus, increase the density. For example, in one test, using very careful extrusion and firing conditions, small-diameter graphite rods with a density of 1.84 gm/cm³ were made from a fine-grained coke flour. The replacement of 20% of the coke flour with furnace black yielded a product with a density of 1.91 gm/cm³.

With the addition of furnace black, graphite with densities greater than 1.90 gm/cm³ can be made consistently in sizes up to 1 inch in diameter. Making larger sizes of graphite of this density by the inclusion of furnace black is very difficult because of the problems involved in processing stock of such low permeability, but work is progressing in this direction.

Flake natural graphite is also of interest as a material for reactor use because it will compact into very dense shapes. Densities as high as 2.15 gm/cm³ have been achieved in molded blocks 6 × 5 × 3 in. in size. Such graphite is inherently very weak because of the plasticity of the flake graphite, but could be used where it is subjected to compressive stresses only.

Grain Size of Petroleum Coke

The reactor graphite discussed above has a maximum particle size of 1/32 in. In making larger graphite shapes usually a greater particle-to-flour ratio and larger sizes of particles (up to ½ in.) are used. The larger particles are able to take up greater thermal strains without rupture and make it easier to process the large-size graphite. Furthermore, graphite arc furnace electrodes can more easily resist the thermal shock conditions to which they are exposed if they contain 40% to 60% of particles blended with the flour component. On the other hand, where fine machining involving sharp edges or very high strength is required, grain sizes much smaller than those given in Fig. 1 may be used.

With regard to the effect of grain size on physical properties, one may make two generalizations. The strength of the stock increases as the grain size is reduced, and the ratio of the properties measured parallel and perpendicular to the grain is increased. The following Table XII illustrates these points, although the stocks used as a basis are not entirely comparable aside from the grain size. For example, the coarse-grained material was not given a pitch impregnation, so that its density is lower than that of the others.

Table XII. Effect of Grain Size on Properties

	Fine grain stock	*Medium grain stock*	*Coarse grain stock*
Bulk density (gm/cm³)	1.64	1.66	1.49
Specific resistance (milliohm-cm)			
Parallel to grain	0.86	0.69	0.96
Perpendicular to grain	1.62	1.12	1.35
Coefficient of thermal expansion ($\times 10^{-7}$/°C)			
Parallel to grain	11	15	16
Perpendicular to grain	41	33	26
Elastic modulus (10^6 lb/in²)			
Parallel to grain	1.84	1.47	0.89
Perpendicular to grain	0.78	0.76	0.61
Flexural strength (lb./in²)			
Parallel to grain	4520	2220	1280
Perpendicular to grain	3000	1630	990

Effect of Calcination Temperature of Petroleum Coke

As indicated above, the raw petroleum coke is normally calcined to a temperature of about 1300°C to preshrink the coke, and thus, avoid processing difficulties. When a lower calcination temperature is used, the properties of the finished graphite are affected markedly. Presumably, this is a result of simultaneous shrinkage of the bond carbon and coke, resulting in a tighter knit structure. The following data in Table XIII, showing the effect of calcining temperature were obtained on small diameter, fine-grained test rods with all properties measured parallel to the grain. Each figure given represents an average over five different petroleum coke sources.

Method of Forming

The effects on orientation of particles of the two general forming methods in common use, extrusion and molding, were discussed in a previous section.

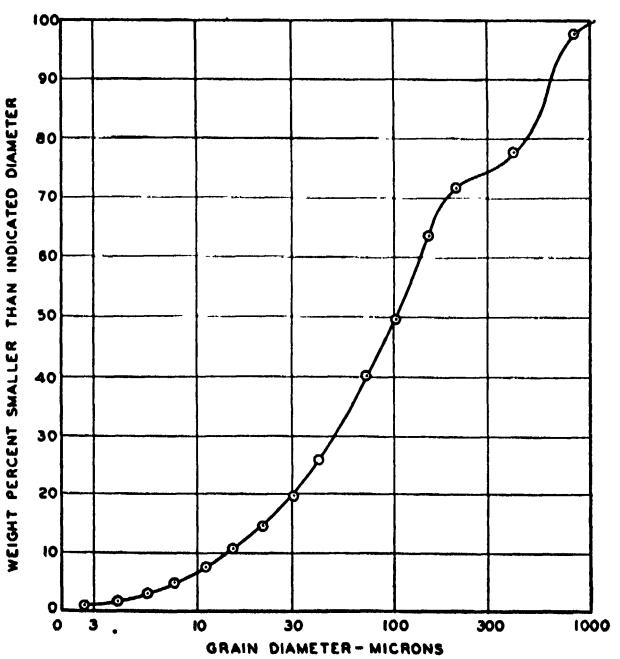


Figure 1. Grain size distribution petroleum coke blend for reactor graphite

The following Table XIV compares the average properties of two fine-grained graphite stocks, one extruded and one molded. It is apparent that extrusion produces a greater degree of anisotropy than molding.

Table XIII. Effect of Coke Calcining Temperature on Graphite Properties (Downey)[9]

	Coke calcining temperature		
	750°C.	*1050°C*	*1400°C*
% volume shrinkage, green to graphite	19.5	9.9	4.0
Bulk density (gm/cm³)	1.55	1.53	1.50
Specific resistance (milliohm-cm)	0.83	0.94	1.00
Coefficient of thermal expansion ($\times 10^{-7}$/°C) at 60°C	19.7	16.1	14.8
Elastic modulus (10^6 lb/in²)	1.52	1.33	1.09
Flexural strength (lb/in²)	3190	2130	1520

Table XIV. Effect of Molding vs. Extrusion on Physical Properties of a Fine-Grained Stock

	Extruded stock	*Molded stock*
Density	1.64	1.75
Specific resistance (milliohm-cm):		
Parallel to grain	0.86	0.96
Perpendicular to grain	1.62	1.32
Ratio	1.88	1.38
Coefficient of thermal expansion ($\times 10^{-7}$/°C):		
Parallel to grain	11	19
Perpendicular to grain	41	32
Ratio	3.70	1.68
Elastic modulus (10^6 lb/in²):		
Parallel to grain	1.84	1.39
Perpendicular to grain	0.78	0.96
Ratio	2.40	1.45
Flexural strength (lb/in²):		
Parallel to grain	4520	4680
Perpendicular to grain	3010	3940
Ratio	1.46	1.25

The orientation of particles in forming is purely mechanical, depending on the shape of the particle. X-ray diffraction studies have shown that there is also an orientation of crystal axes, stemming from the tendency of the layer planes of the graphite crystal to lie parallel to the long dimension of the coke particle. Magnetic susceptibility measurements on pure graphite samples provide an easy measure of the extent of crystal axis alignment, to separate it from the purely mechanical particle alignment. Ganguli and Krishnan[10] showed that graphite crystals have a large diamagnetic susceptibility when the magnetic field is perpendicular to the layer planes, and a very small value for this property when the magnetic field is parallel to the layer planes. Since the susceptibility does not depend on the way in which the crystals are joined together, it can be used to get a true idea of the distribution of crystal orientation. Table XV gives the results of such magnetic susceptibility measurements on a molded and an extruded fine-grained stock, in comparison with other bulk physical properties.

Effect of Final Firing Temperature

A remarkable change in physical properties occurs when the gas-fired carbon is heated to temperatures of 2500°C to 3000°C. Nearly all of the changes are due to the increased perfection of the graphite crystals, which are quite disorganized in the gas-fired state. These crystal changes will be discussed in some detail in a later section, so that we will note here only the gross over-all property changes that take place when gas-fired stock is graphitized.

The most obvious physical changes that accompany graphitization are those of appearance and hardness, and although these properties are scarcely suitable for a scientific definition of graphite, they can be used with reasonable accuracy by experienced men to determine the quality of the graphite. For example, when a knife is rubbed over the surface of a piece of carbon, it will expose a dark grey or black surface and the surface will feel gritty. With graphite, a shiny light grey surface will be exposed, and the surface will feel smooth and somewhat greasy to the touch. Gas-fired carbon is very hard and brittle and is one of the most abrasive of materials. It cannot be cut with any kind of steel without dulling the tool very rapidly. For example, a high-speed tool steel bit will become noticeably dull after 100 linear inches of cut in gas-fired carbon stock; whereas the same piece of carbon after graphitization will require perhaps 10,000 linear inches of cutting to produce the same degree of wear on a tool bit made of soft brass. Another way of stating this extreme difference of hardness is that the gas-fired carbon requires a diamond saw to cut it; whereas graphite made from petroleum coke can be machined with woodworking tools. When accurate and easy machining is required, it is important that the final firing temperature be at least 2500°C.

Changes in physical properties on graphitization include a decrease of specific resistance by a factor of five, an increase of thermal conductivity by a factor of twenty-five, a 50% decrease in coefficient of thermal expansion, and a 20% decrease in elastic modulus and in strength. It is interesting to note that all of these changes, except that of thermal expansion, take place in the reverse direction on exposure of graphite to fast neutrons.

Table XV. Crystal Orientation as Affected by Forming Method

	Graphitized extruded stock	*Graphitized molded stock*
Magnetic susceptibility $\times 10^6$:		
Field parallel to grain	4.05	(*a*) 6.31 (*b*) 6.20
Field perpendicular to grain	(*a*) 8.17 (*b*) 7.76	7.87
Average ratio	2.02	1.25
Specific resistance (milliohm-cm):		
Parallel to grain	0.706	0.96
Perpendicular to grain	1.12	1.36
Ratio	1.59	1.43
Elastic modulus 10^6 lb/in^2:		
Parallel to grain	2.29	1.16
Perpendicular to grain	0.832	0.708
Ratio	2.75	1.64

PHYSICAL PROPERTIES

The commercial graphite used for reactors is a mixture of crystalline graphite and cross-linking intercrystalline carbon, and the physical properties that are measured are the result of contributions from both sources. Ideally, it would be desirable to analyze the fundamental physical properties in terms of the relative contributions of the two components. To date, it has been possible to study the the theory of only the crystalline graphite in any quantitative fashion, and the result is that only those properties which are not primarily determined by the intercrystallite structure can be discussed quantitatively. Thus, a discussion of physical properties starts with the examination of single crystal properties, and the properties of bulk graphite are related to these when possible. It is not intended that this discussion should be exhaustive, since the literature already contains several good surveys.[11]

Crystal Structure

The graphite crystal structure consists of layer planes of hexagonally arranged atoms with tight binding in the planes and loose binding between the planes.

In the normal structure described by Bernal,[12] alternate layer planes are similarly placed, as indicated schematically in Fig. 2. Alternate structures for graphite are discussed adequately by Howe.[11]

X-Ray Studies of Graphitization

Natural graphites and graphites made by the decomposition of carbides have large crystallites of nearly perfect structure, and in consequence, have sharply defined X-ray lines as expected from the crystal structure indicated in Fig. 2. The graphitiza-

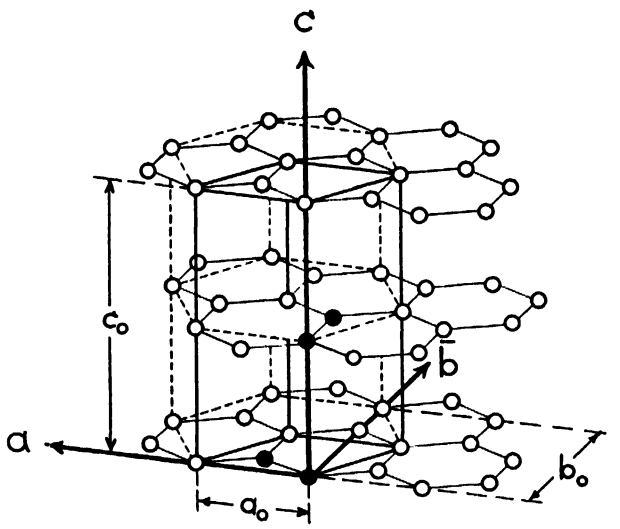


Figure 2. Classical graphite lattice: *a*, *b* and *c* are the orthohexagonal axes; the hexagonal unit cell, to which the four black atoms are assigned, is outlined by solid lines; $a_0 = 2.46$ Å; $b_0 = 4.28$ Å; $c_0 = 6.71$ Å

tion process (heating to 3000°C) applied to petroleum coke, develops the graphite crystal structure to varying extents, but never quite to the perfection exhibited by natural graphite.

In general, this process of graphitization can be divided into three steps. The first step is the heating of the petroleum residue to 450°C, which causes the planar aromatic systems to polymerize and become rigid. At this step, X-ray examintion shows a general layering of the aromatic planes.

The second step occurs on heating to say 2000°C during which there is a pronounced evolution of gas accompanied by a growth of the planes. At this point, although the particle size may be considerable, the properties characteristic of completed graphites are not observed. The generally accepted model is that, although there are deep stacks of parallel planes, there is little ordering of these planes with respect to each other.

The ordering of these planes according to the alternate layer stacking shown in Fig. 2 occurs in the third or final stage of graphitization in which the carbon is heated to 3000°C. The study of this final graphitization step has been the subject of much effort using X-ray diffraction methods, and some of the recent results will be given after a comment on the method of analysis of the X-ray data and a description of the model that is assumed.

The simple application of X-ray line widths as a measure of crystal size is of qualitative value only. For a quantitative study, the X-ray line shapes must be subjected to a Fourier analysis to separate strain broadening from particle size broadening and stacking fault effects, according to the method used by Warren[13] and others.

A model that is compatible with the X-ray data was proposed by Franklin,[14] and has been used by Houska and Warren,[15] and Bowman[9] on different samples. The model simply assumes that adjacent layer planes either have the correct graphite relation to each other, or they are randomly oriented. Further, if they have the correct graphite relationship, the interlayer spacing is $a_3 = 3.35$ Å, and if adjacent planes are randomly oriented, their interlayer spacing is $a_3' = 3.44$ Å. Imperfect graphites are then assumed to be composed of a mixture of pairs of planes of correct and random orientation, statistically distributed along the *c*-axis of the crystal.

With these assumptions it is possible to calculate the probability P that adjacent pairs of planes are properly oriented in essentially three independent ways; these are: first, the apparent planar spacing $\bar{a}$, as measured from the $(00l)$ reflection is simply the weighted average of the two discrete spacings, $\bar{a}_3 = Pa_3 + (1 - P)a_3'$. Second, the analysis of shape of the broadened $(00l)$ lines will yield knowledge of the randomness of layer spacing, giving a value for $(1 - P)a_3'$. Finally, analysis of the more complex (hkl) reflection also leads to a value of P.

Warren and Houska applied this analysis to a carbon black, heat treated at 2300°C and found the probability P of the correct graphite orientation to be only 0.25. This problem has been studied by Pattin and Bowman, who obtained values of P as a function of baking temperature for both coke and lampblack. This value of P for lampblack stock fired to 3000°C was about 0.33. This low value is in agreement with the well-known difficulty of producing perfect graphite from this material. On the other hand, coke stock is known to be much more susceptible to graphitization, and Bowman's observations, as listed below, certainly check this.

Firing temperature, °C	*P (probability of ordered plane pairs)*
2000	0.20
2200	0.55
2400	0.73
2600	0.82
2800	0.89
3000	~ 1.00

In summary, it can be said that the model of ordering of stacked parallel planes, accompanied by a change of layer spacing from 3.44 Å to 3.35 Å, seems to have rather general validity.

Thermal Properties

It is convenient to divide the discussion of thermal properties in each case into the high- and low-temperature regions relative to room temperature. In the very low temperature region, the intrinsic anisotropy of crystalline graphite is evident, not only in the directional anisotropy of some of the thermal properties, but also in the manner in which these vary with temperature; in the high-temperature region, while the directional anisotropy remains, the variation of properties with temperature is not particularly anomalous. Specific properties will now be discussed.

Specific Heat

In the high-temperature region, the specific heat C_P rises smoothly from a value of 2.05 cal/gm atom-deg. at 300°K to a value approaching the classical value of approximately 6 cal/gm atom-deg. at about 2000°K. The data are available in the literature[16] and are summarized in Table XVI.

Table XVI. Selected Values of C_p cal/gm atom-deg.

T°K	C_p	T°K	C_p
300	2.05	1000	5.14
500	3.49	1250	5.53
750	4.48	1500	5.75

In the low-temperature region, there has been much recent interest, both theoretically and experimentally. The significant experimental feature is that the specific heat varies very nearly as T^2 over the temperature range of about 20-60°K.[17] In the lower temperature region, 1.5-10°K, the variation seems to be as $T^{2.4}$. The theory of this behavior is still a matter of discussion, but the general features are understood.

The T^2 dependence of the specific heat at low temperatures can be explained from two different ways of treating the vibration spectrum of anisotropic materials such as crystalline graphite. On the one hand, purely geometric considerations (Krumhansl and Brooks)[8] lead to a straight-forward modification of a simplified Born-von Karman treatment which results in a spectrum approximately characteristic of a two-dimensional system (C_V proportional to T^2). On the other hand, Komatsu and Nagamiya[19] considered the out-of-plane vibrations as the bending vibrations of a plate. Whereas, the elastic spectrum of an infinite body has the usual frequency (f) and wave length (λ) relation $f\lambda = v$ where v is an essentially constant velocity of propagation, for bending waves the relation becomes $f\lambda^2 = c$, and the group velocity $df/[d(1/\lambda)]$ is not constant, but varies as $f^{0.5}$, a profound modification in the vibration spectrum. The above, while a simplification, is the essence of the problem; when extended carefully to three-dimensional graphite, it leads also to a T^2 dependence of C_p.

The two points of view can be reconciled and recent independent studies by Newell[20] and Fatherly and Krumhansl[21] have shown that, in reality, both features are probably present. The "bending" modes associated with bond bending lead to a particularly strong "next nearest neighbor" interaction of the sort which gives a spectrum closely similar to that obtained from the plate-bending approximation. Thus, it can be said that the general features of the specific heat are understood and semi-quantitative agreement with experiment can be obtained using benzene molecular force constants in a Born-von Karman calculation starting from first principles. In closing this section, it might also be noted that the specific heat does not vary much from one graphite to another, although there are small, but real differences between grades in the low-temperature region.

Thermal Conductivity

Artificial graphite has an unusually high thermal conductivity, especially at room temperature. The thermal conductivity parallel to the grain is comparable with aluminum, and perpendicular to the grain, it is comparable to brass.

Unlike metals, the heat current in graphite is carried by the lattice vibrations, and the monotonically decreasing thermal conductivity above room temperature is consistent with this assumption. The lattice thermal conductivity is given by*

$$K = \gamma C_v l v$$

where K = thermal conductivity, γ = geometric factor (⅓ in isotropic media), C_v = specific heat, l = suitably averaged mean free path, and v = suitably averaged lattice wave group velocity. In the high-temperature regions above 1000°C, except for l which is expected to vary as T^{-1}, these quantities vary slowly with temperature—in general agreement with experiment.

A number of thermal conductivities at room temperature and above for Acheson graphite are reported in the literature, some of them quite accurately determined, but few literature references give sufficient information on the other properties of the particular graphite examined to characterize it properly. Johnson[9] has measured the thermal conductivity of a number of graphite grades, as given in Table XVII following, and noted that within the accuracy of his thermal conductivity measurements, there was a one-to-one correspondence between electrical and thermal conductivity. A recalculation of Johnson's data, converting the measurement of thermal conductivity to 25°C, gives a value of 0.00030 for the product of the resistivity in ohm-cm and the thermal conductivity in calories/sec-cm-°C. (This product has no relation to the Wiedemann-Franz law, because the thermal conductivity is not electronic in nature.)

Similarly, Neubert[22] noted this one-to-one relationship of thermal and electrical conductivity. Some of his general measurements of thermal conductivity are given in Table IX, but his accurate determination of the constancy of the ratio of thermal conductivity and electrical conductivity was accomplished by measuring both properties on a number of individual samples of widely varying conductivity. According to Neubert, the product of the resistivity in ohm-cm and the thermal conductivity in cal/sec-cm-°C is 0.00032 when both are measured at room temperature.

The data of Powell[23] and Powell and Schofield[24] allow the calculation of this product for four of their

* In exact form for anisotropic media, this is a tensor equation.

Table XVII. Thermal Conductivity of Graphite (Parallel To Grain)

Coke source	Diameter of original extruded piece (in.)	Maximum size particle in mix (in.)	Pitch impregnated	Mean t° of K determination	Thermal conductivity cal/sec-cm-°C	25°C specific resistance milliohm-cm	$K\rho \times 10^3$
A	18	1/8	no	58.8	0.268	1.090	0.281
A	18	1/8	no	58.0	0.258	1.176	0.303
A	12	1/16	no	57.4	0.274	1.115	0.305
A	3	1/32	no	54.0	0.324	0.911	0.295
A	3	1/32	yes	47.3	0.428	0.663	0.284
A	4	1/32	no	59.3	0.257	1.118	0.305
A	4	1/32	no	50.8	0.382	0.748	0.286
A	2	flour only	no	45.7	0.357	0.827	0.295
A	2	flour only	yes	46.2	0.370	0.788	0.291
B	18	1/8	no	53.3	0.341	0.844	0.288
B	12	1/16	no	52.7	0.355	0.791	0.281
B	4	1/32	no	51.7	0.364	0.806	0.293
B	2	flour only	no	46.1	0.400	0.684	0.274
B	2	flour only	yes	42.0	0.51	0.546	0.278
C	12	1/16	no	56.8	0.353	0.809	0.286
C	4	1/32	no	49.5	0.415	0.688	0.286
C	2	flour only	no	45.1	0.397	0.722	0.286
C	2	flour only	yes	44.9	0.375	0.830	0.311
D	2	flour only	no	42.6	0.419	0.684	0.286
D	2	flour only	yes	46.9	0.409	0.718	0.293
E	2	flour only	5 times	40.1	0.451	0.654	0.295

samples. The average for these four samples yields a product $K\rho$ of 0.000307. Micinski[9] made a direct measurement of the product $K\rho$, using Kohlrousch's method of determining thermal conductivity, and his average value for two graphite stocks was 0.000323 at 25°C.

This survey showing the relative constancy of the product of thermal conductivity and resistance covers a wide range of graphites, with conductivities ranging over a factor of more than 2. It is believed to be general enough in validity to justify the use of the relationship in calculating the room temperature thermal conductivity of graphite from the room temperature resistance which is easy to measure accurately. If the relation: K(in cal/cm-sec-°C) times ρ (in ohm-cm) equals 0.00031 is used for measurements at 25°C, it is believed that the calculated thermal conductivity will be accurate to within 5%.

The variation of thermal conductivity with temperature has been measured by a number of workers. Some of the more reliable of these are plotted in Fig. 3, with all data replotted as a percentage of the 25°C value. Where the 25°C value was not available, it was calculated from the resistance of the sample, if it was available in the same grain orientation as the thermal-conductivity measurement. It is to be expected that there will be some variation in the ratio of high-temperature thermal conductivity to room temperature values, and the curve gives some support for this view. However, the trend of thermal conductivity with temperature is obvious.

In addition to those shown, there are a number of other measurements by Micinski and Gardner,[9] made with an elaboration of Powell and Schofield's high-temperature method, that indicate that the thermal conductivity of petroleum coke graphites in the direction perpendicular to the grain lies between 0.055 and 0.08 cal/sec-cm-°C in the temperature range of 1500°C to 1900°C. The thermal conductivity parallel to the grain should exceed these values, and in support of this view, Jain and Krishnan's value at 1825°C is 0.096 cal/sec-cm-°C.

From a practical standpoint, the behavior of K below room temperature may at first seem to be unimportant, but it now appears that much useful information about the structure of graphite and the effects of radiation damage[26] can be obtained by a study of the thermal conductivity at temperatures below 100°K.

Recently, Smith[27] has measured experimentally the low-temperature thermal conductivity of several

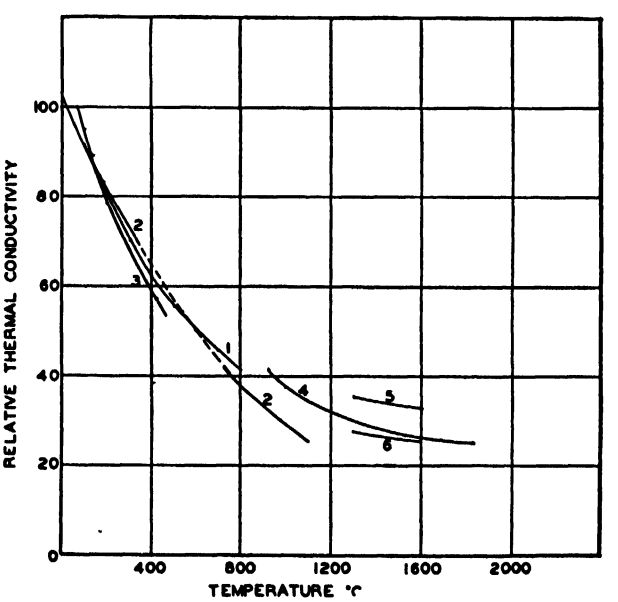


Figure 3. Temperature dependence of the thermal conductivity of graphite; curve 1: Powell;[28] curve 2: Powell and Schofield;[24] curve 3: Odening and Zaffarano;[9] curve 4: Jain and Krishnan;[25] curves 5 and 6: Micinski and Downey[9]

well-crystallized natural and artificial graphites and found that it varied approximately as the specific heat, *i.e.*, as the square of the temperature. This is to be expected at low temperature if the mean free path l is determined by boundary scattering and is, therefore, constant. Earlier measurements in other graphites showing that the thermal conductivity varied as some higher power of T ($T^{2.7}$ to T^3) are now interpreted as resulting from the sensitivity of the thermal conductivity to the details of the connections between particles.

In commercial graphite, it seems possible to treat phenomenalogically the thermal resistance as the sum of the crystalline resistance and the resistance of the intermediate cross-linking carbon, with the latter playing the major role. The general features of thermal conductivity in the low temperature region as measured by Smith[27] are shown in Fig. 4.

Thermal Expansion of Graphite

The thermal expansion of crystalline graphite is extremely anisotropic. Using X-ray diffraction methods, Nelson and Riley[28] measured the thermal expansion of finely-ground Ceylon graphite (4% ash) from 15°C to 800°C. They found that the thermal expansion along the a-axis of the crystal was negative at room temperature, with a value of -15×10^{-7}/°C over the temperature range of 0–150°C. The expansion becomes more positive with increasing temperature becoming zero at approximately 400°C and having a mean value of $+9 \times 10^{-7}$/°C over the temperature range 600–800°C. The expansion in the c–axis crystal direction was quite large, a mean coefficient of 283×10^{-7}/°C being obtained over the temperature interval 15°C to 800°C.

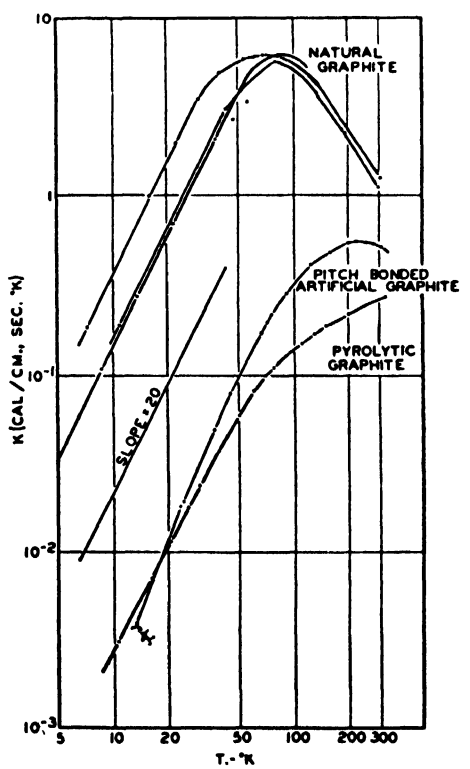


Figure 4. Low-temperature thermal conductivity of graphites

Using somewhat less perfectly crystalline, but purer graphite (artificial graphite from petroleum coke), Walker, McKinstry and Wright[29] made very careful X-ray diffraction measurements of the c-axis layer plane spacing from — 196°C to 1118°C. They found that the change in spacing was linear with temperature over this range, leading to a coefficient of thermal expansion of $286 \times^{-7}$/°C, in excellent agreement with Nelson and Riley.

Bowman[9] has measured by X-ray diffraction the difference in c-axis expansion between petroleum cokes of quite different degrees of crystal size and perfection. The difference of crystal perfection was obtained by heat treating one coke to only 2000°C and the other coke to 3000°C. The 2000°C treated sample had a c-axis spacing of 3.41 Å and the 3000°C treated sample had a c-axis spacing of 3.36 Å. The crystal size of the two samples were 160 Å and 600 Å, respectively, parallel to the c-axis. Despite these differences, there was no detectable difference in c–axis thermal expansion between the two samples over the temperature interval 20° to 200°C within the accuracy of the experiment, namely, 2 parts in 1000, so that crystal perfection has little effect on thermal expansion of graphite crystals.

Any relationship between the bulk thermal expansion of graphite and that of the crystals of which it is composed is secondary, to say the least. For example, carbon blacks made from the coke used in Bowman's experiment and heat treated to the two temperatures would have quite different thermal expansion coefficients. The volume thermal expansion, calculated by addition of the linear coefficients measured in three mutually perpendicular directions, would be 87×10^{-7}/°C for the 2000°C coke and 56×10^{-7}/°C for the 3000°C coke, a difference of 35%. Furthermore, these volume expansions of bulk graphite, and volume expansions calculated from the linear expansions given in Tables IX, XI, XII and XIV are much lower than the volume crystal expansion of 253×10^{-7}/°C calculated from Nelson and Riley's data.

The only easily apparent relationship of bulk to crystal expansion is that the anisotropy of linear expansion coefficients for bulk graphite is undoubtedly caused by the anisotropy of the graphite crystal expansions. For example, the thermal expansion of 3000°C heat-treated petroleum coke particles has been measured by Micinski[9] using an interferometer method. The particles were selected as having a particularly striated appearance, and the measurements were made parallel and perpendicular to these striations. Parallel to the striation, the thermal expansion coefficient was about -6.5×10^{-7}/°C over the temperature range 0 to 150°C as compared with Nelson or Riley's -15×10^{-7}/°C for the crystal expansion along the a-axis. The thermal

expansion coefficient of the particles becomes zero at about 250°C and becomes positive above this temperature. Perpendicular to the striation, the thermal expansion coefficient was only 20 × 10^{-7}/°C showing little effect of the high *c*–axis expansion.

To obtain the dimension changes of graphite at high temperature, data are needed for the change of mean coefficient of linear expansion with temperature. Using two methods for measuring the differential expansion of different kinds of graphite, Dexter[9] has shown that the change in coefficient of expansion with temperature must be very nearly the same for different types of graphite. The data in Table XVIII are typical of his measurements.

The values in the temperature range 15–100°C were determined by clamping a 6-in. length of the sample graphite to a similar length of the reference graphite at one end and measuring the differential expansion of the other end by noting the rotation of a mirror mounted on a cylindrical rod separating the two graphites. The measurements over the higher temperature intervals were made by inserting a 6-in. length of the sample graphite in a capsule made of the reference graphite. The capsule had a tight-fitting plunger of the reference graphite against the sample, and the distance that this plunger was pushed out of the capsule by the graphite sample when the assemblage was heated was a measure of its total expansion over the temperature interval.

Since the values in the preceding table are relative to the reference stock, they represent only the difference between the mean expansion coefficient of the test graphite and the expansion coefficient of the reference stock. Later it will be shown that the mean expansion of the test graphite can be expected to increase by 29.2 × 10^{-7}/°C in going from the left-hand to the right-hand column of Table XVIII. In contrast with this, the reasonable constancy of the differential thermal expansion coefficients in Table XVIII over the wide temperature range noted is quite good proof that, at least for engineering purposes, the change of thermal expansion coefficient with temperature is the same for all samples tested as it is for the reference graphite.

The most accurate measurements of the variations of thermal expansion coefficient with temperature over the temperature range up to 600°C have been done with an interferometer method patterned after Merritt's work.[30] Figure 5 gives results of mean thermal expansion coefficient measurements for three widely different types of graphite between room temperature and the final temperature indicated.

The circled points were obtained by bringing the furnace to equilibrium at that temperature, and the dotted points were obtained from readings while the furnace was being heated. The points at the higher temperature are more accurate since their calculation involves a wider temperature interval and they have been weighted more heavily than the lower temperature points in drawing the curves. The slope of the curves is approximately the same for all three graphites (and many others tested), in agreement with Dexter's observations.

Thermal expansion measurements at temperatures up to 2500°C have been made on a number of graphites by Westbrook and Micinski.[9] Twelve-inch long samples were mounted in a four-inch id graphite resistance tube furnace, and length changes were determined by telemicroscopic observation of pointed tungsten probes mounted ten inches apart in the sample. An apparatus of considerable physical and thermal stability was required, yielding measurements with an accuracy of ± 0.0002 inch expansion and ± 5°C. Figure 6 gives the results obtained on four widely different kinds of graphite, all measured parallel to the axis of extrusion. Obvious small

Table XVIII. Differential Thermal Expansion of Various Graphite Samples

Graphite sample no.	*Orientation**	*Mean differential coefficent of thermal expansion relative to reference stock†/°C × 10^{-7}*			
		Temperature interval			
		15-100°C	*25-1000°C*	*25-2300°C*	*25-3000°C*
170	Parallel	5.8	5.6	4.4	–
	Perpendicular	19.4	21.5	22.1	–
177	Parallel	7.5	6.2	6.7	4.1
	Perpendicular	23.3	23.6	24.1	–
173	Parallel	1.6	0.6	–	0.2
	Perpendicular	21.9	21.7	–	–
178	Parallel	23.7	24.6	24.9	27.9
	Perpendicular	34.5	33.0	38.8	–
193	Parallel	7.5	9.1	6.2	–
	Perpendicular	20.6	21.3	22.2	–
194	Parallel	6.4	8.1	6.5	–
	Perpendicular	19.6	21.3	22.0	–

* Parallel or perpendicular to grain.

† Reference stock is fine-grained graphite of unusually low thermal expansion coefficient.

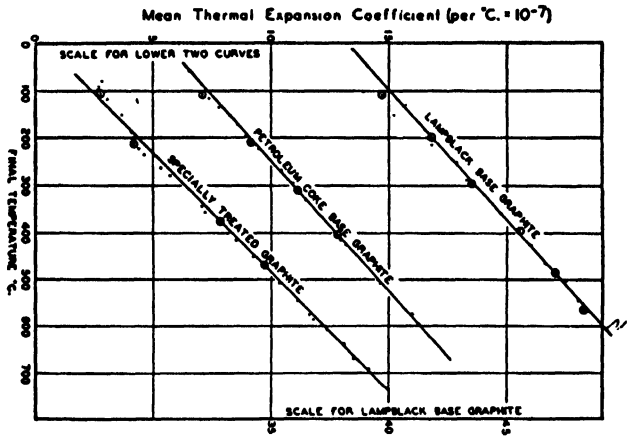

Mean Thermal Expansion Coefficient (per °C. × 10⁻⁷)
SCALE FOR LOWER TWO CURVES
PETROLEUM COKE BASE GRAPHITE
LAMPBLACK BASE GRAPHITE
SPECIALLY TREATED GRAPHITE
SCALE FOR LAMPBLACK BASE GRAPHITE

Figure 5. Mean thermal expansion coefficient by the interferometer method

irregularities of expansion occur in individual samples, probably as a result of irregular release of internal stresses. Nevertheless, the parallel nature of the curves is consistent with the idea that the change of thermal expansion coefficient with temperature is approximately the same for all graphites.

This idea leads to a simplification for engineering purposes of the calculation of high-temperature thermal expansion. It has been found that the mean linear coefficient of thermal expansion between room temperature and any final temperature can be obtained from the value for the temperature interval—room temperature to 100°C—by adding to it the numbers shown in the Table XIX. This is valid for stock of any orientation. Using the table, the expansion curves of individual graphite samples can be computed to obtain good agreement with the measured curves.

Hidnert[31] has published some very accurate thermal expansion values for graphite. The variation

Table XIX. Calculation of Mean Coefficient of Thermal Expansion

Final temperature °C	*Value to be added to coefficient/°C determined over temperature range 20°C — 100°C × 10⁻⁷*
100	0
200	2.0
300	4.0
400	6.0
500	7.7
600	9.2
700	10.4
800	11.4
900	12.3
1000	13.2
1500	17.2
2000	21.2
2500	25.2

of mean coefficient of thermal expansion with temperature reported by him agrees very well with the variation calculated from Table XIX up to the limit of Hidnert's measurements, namely 1000°C.

Studies of thermal expansion of graphite at low temperatures have not been made as yet.

Vapor Pressure, Heat of Sublimation, and Fusion

The heat of sublimation of graphite has been a subject of debate for many years, and the resolution of the problem has been slow because of the difficulty of carrying out unambiguous experiments at high temperatures. However, there now seems to be a growing agreement on a value of 170.4 kcal per mol, as a result of the general agreement of vapor pressure determination by several groups.[32]

Vapor pressure determination requires a knowledge of the molecular species evaporated, and in some cases, a knowledge of the accommodation coefficient or "sticking factor" for carbon atoms striking the surface. Both of these are still under some debate.[33]

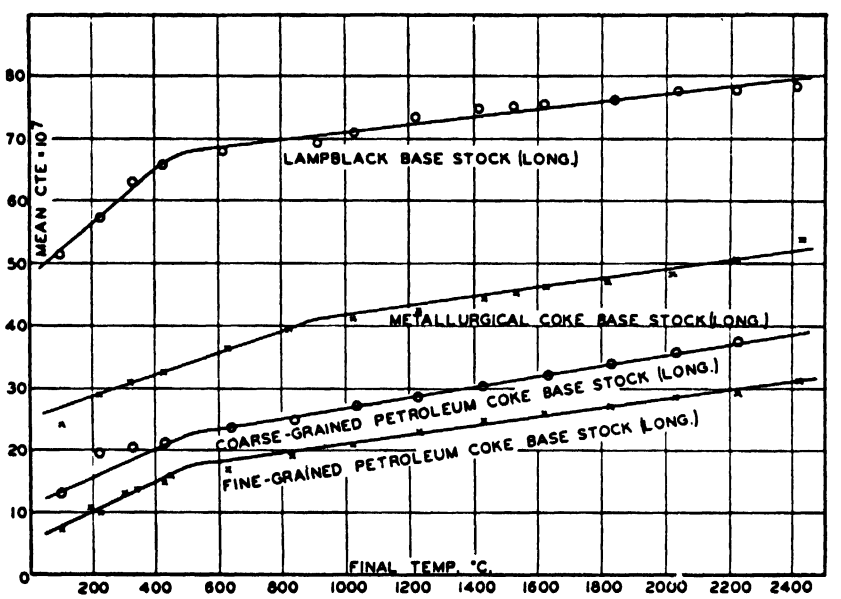

MEAN CTE × 10⁷
LAMPBLACK BASE STOCK (LONG.)
METALLURGICAL COKE BASE STOCK (LONG.)
COARSE-GRAINED PETROLEUM COKE BASE STOCK (LONG.)
FINE-GRAINED PETROLEUM COKE BASE STOCK (LONG.)
FINAL TEMP. °C.

Figure 6. Mean coefficient of thermal expansion of graphites by an optical dilatometer method

Most experimenters, however, hold that the accommodation coefficient is reasonably high, so that effusion experiments give a good representation of the vapor pressure. Mass-spectrometer determinations indicate the presence of the molecular species C_1, C_2, C_3 with higher molecular clusters possible in the vapor from graphite. Most vapor pressure measurements are consistent with a vapor pressure of approximately 5×10^{-6} atmospheres at 2500°C, and their extrapolation leads to a sublimation point at atmospheric pressure of greater than 4400°K. This is a much higher temperature than the accurately determined carbon arc crater temperature,[34] which is usually assumed to be close to the sublimation point.

The triple point of graphite has been reported by Basset[35] to occur at 105 atmospheres pressure and 4000°K. Jones[9] has recently used an arc operating in argon at 150 atmospheres to melt graphite. The graphite, thus recrystallized from the melt, is of nearly perfect crystal structure (micro-crystals) and high purity and density.

Emissivity

Since graphite is used for many high-temperature applications where heat transfer by radiation is dominant over transfer by convection, the emissivity of graphite is an important number. As can be expected with any high-temperature measurement, perfect agreement has not been obtained among various observers. Furthermore, the emissivity of graphite varies with the surface finish, and even when starting with a polished surface, prolonged heating at high temperatures will change the character of the surface and increase its emissivity.

Figure 7 gives the results of a number of measurements of graphite emissivity. It is likely that the measurements of Thorn and Simpson[36] are the most accurate that have been made, and these point to a value between 0.77 and 0.78 for polished graphite. Their points at 0.905 were obtained after prolonged evaporation and clearly indicate the effect of surface conditioning.

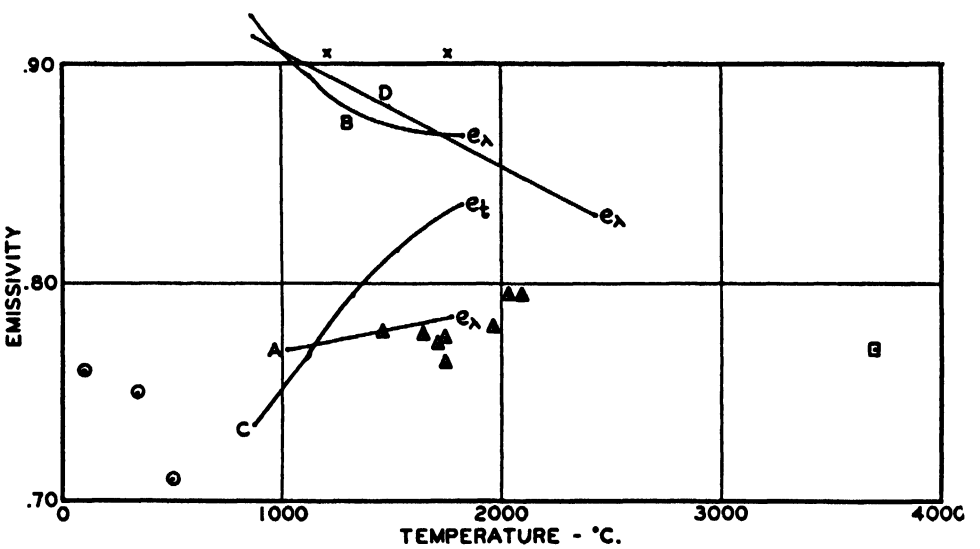
Micinski's[9] values and those for the arc temperature are calculated with the assumption that the spectral and total emissivity are the same. Spectral energy distribution curves at the arc temperature[34] indicate either that $e_\lambda = a/\lambda$ is constant with wavelength, or that its wavelengtn dependence is of the type log $e_\lambda = a/\lambda$. Since there is no *a priori* reason for the latter dependence, the simpler assumption is that the emissivity is independent of wavelength, and therefore, that the total and spectral emissivities are the same.

A general conclusion from Fig. 7 would be that the emissivity of graphite lies between 0.75 and 0.90, with the exact value depending on the nature of the surface.

Electrical Properties

Resistivity

Single crystals of graphite are highly anisotropic in resistance as in other properties. Parallel to the planes, the resistivity at room temperature is about



⊙ BARNES, FORSYTHE AND ADAMS: TOTAL EMISSIVITY, ROUGH SURFACE
A THORN AND SIMPSON: SPECTRAL EMISSIVITY, POLISHED SURFACE
× " " " : " , CONDITIONED SURFACE
B JAIN AND KRISHMAN: " " , "
C " " " : TOTAL EMISSIVITY, "
▲ MICINSKI: TOTAL AND SPECTRAL EMISSIVITY, SMOOTH SURFACE
⊡ MACPHERSON: " " " , ARC ANODE
D PRESCOTT AND HINKE: SPECTRAL EMISSIVITY

Figure 7. Emissivity of graphite

5×10^{-5} ohm-cm,[37] and perpendicular to them, it is 100 to 1000 times this. The values of resistance for multicrystalline artificial graphites are not expected to have any simple relation to those for single crystals, although the anisotropy of resistance of artificial graphite shown in most stocks is, of course, related to the single crystal anisotropy. Values of resistance given for commercial graphites in Table IX indicate that it is about a factor of 20 higher than that of single crystals parallel to the planes.

An interesting plot showing the wide range of possible variations of resistivity in graphites with temperature is given in Fig. 8. Most multicrystalline artificial graphites decrease in resistance with increasing temperature, at least up to 400°C. With petroleum coke base stocks, a minimum in resistance is reached in the range of 400°C to 600°C, and above this temperature the resistance increases almost linearly with temperature. The behavior of artificial graphite in this range is generally attributed to the dominance of lattice vibrations rather than crystal boundaries and imperfection in the scattering of current carriers (electrons and holes).

The curve for single crystal graphite indicates a decreasing resistance as the temperature is lowered. Later it will be indicated that this temperature dependence requires a modification of the band picture. Meers[9] has succeeded in producing an artificial graphite that approaches the single crystal behavior even though it is multicrystalline. The method used for the preparation of the graphite was a pyrolytic one patterned after Meyer's[38] work. The temperature variation of resistance of this pyrolytic carbon is given in Table XX in comparison with single crystals of natural graphite.

It is interesting to note that the similarity of this pyrolytic graphite to single crystalline graphite extends to low-temperature thermal conductivity, both displaying a T^2 dependence.

Table XX

	Electrical resistivity (in metro-ohm-cm) pyrolytic graphite vs natural graphite		
	4.2°K	*77.3°K*	*300°K*
Pyrolytic	25	55	65
Single crystals	5	30	55

Band Structure

The electronic energy band picture of graphite and its relationship to the electrical properties has recently been given a great deal of theoretical and experimental attention,[39] and for a detailed review, the literature should be consulted. According to the simplest picture, graphite is a semiconductor with nominally a zero energy gap between filled and empty bands. Unlike usual semiconductor materials, the density of states does not go to zero at the band edges, but has a small finite value, rising rapidly on entering either band.

For pure graphites, this picture yields equal numbers of holes and electrons. If the electrons and holes had equal mobility, the Hall coefficient would be zero by virtue of the cancellation of the hole and electron contributions. The fact that pure graphite, whether of natural or artificial origin, has a negative Hall coefficient indicates that electrons have a slightly higher mobility than holes.

The ratio of electrons to holes can be varied in graphite by various techniques. Hennig,[40] for example, has shown that chemical doping of graphite with halogens, alkali metals or bisulfate ions changes the electron concentration markedly. Figure 9, taken from data by Westbrook and Pattin[9] shows that it is possible to vary the Hall coefficient of a commercial graphite in the direction of either excess holes or excess electrons with small amounts of additives. Incidentally, an excess of either holes or electrons provided in this way increases the electrical conductivity, as would be expected from the increased number of carriers.

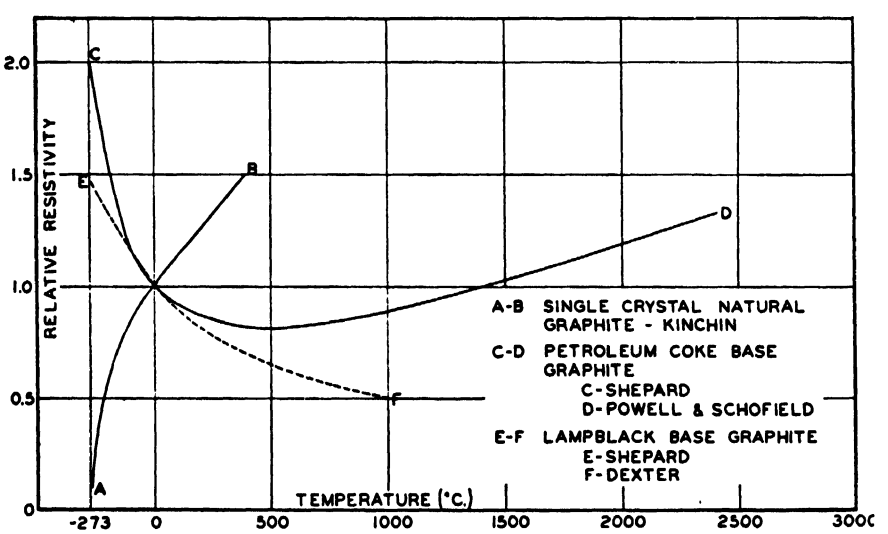


Figure 8. The temperature dependence of electrical resistivity of graphites

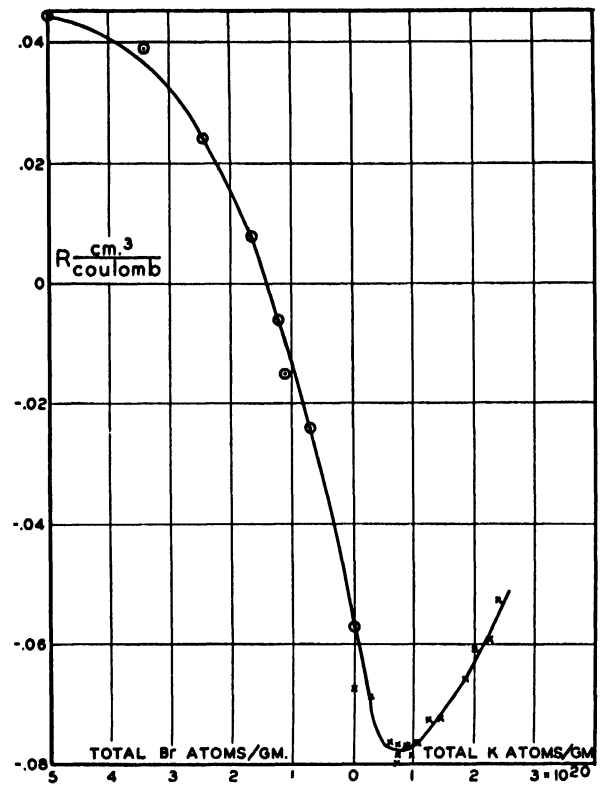


Figure 9. Hall coefficient of graphite with added impurities

The negative value of the Hall coefficient for pure graphite is indicated in Fig. 9. Typical data showing how this value is approached in the firing of a molded coke-base stock to successively higher temperatures is indicated in Fig. 10.

The theoretical studies of band structure indicate that near the band edges, the effective masses of the electrons and holes are small. This finding is in agreement with the anomalously high diamagnetic susceptibility for pure graphite. When the electron concentration is changed appreciably by chemical additives, a more normal value is found for the susceptibility, corresponding to higher effective electron masses away from the band edge.

The band picture described above would lead to the prediction that the resistivity of graphite increases monotonically with decreasing temperature down to absolute zero. While commercial multicrystalline graphite has this behavior, single crystals of natural graphite behave oppositely with their resistance decreasing as the temperature is lowered. Thus, one is led to correct the simple theory to allow for a small overlap (very weakly metallic behavior) of the bands, as postulated by Kinchin[37] and by Johnston.[39]

Other observations, such as the magnetic field dependence of resistance and the Hall coefficient, the extreme sensitivity of the thermoelectric power to sample history and radiation damage serve to bring out clearly the competition between opposing effects in the two-carrier system (electrons-holes) necessary for the description of graphite. Moreover, they all point up the increased precision that will be required of theoretical calculations of electronic energy levels in graphite to bring our knowledge to the quantitative level existing for some other semiconducting materials.

MECHANICAL PROPERTIES

From the description of the method of manufacture, it may be surmised that the mechanical properties of formed graphite will vary from piece to piece of the same grade, and that each piece of graphite will not be uniform throughout its cross section. Property variations of 15–30% across the diameter of a large piece of graphite are not unusual.[41] For this reason, a fairly large number of samples must be measured to get a true picture of the properties of a particular graphite.

Flexural and compressive strengths are easier to measure than crushing strength, and flexural strengths are of more significance for practical use than compressive strengths; consequently, flexural strengths are commonly used for control purposes. Although the most common way of making flexural strength tests is to apply the load at a single point at the center of a beam supported near its ends, the recommended way[42] for brittle materials is to apply the load at two points so that a greater length of the sample is under maximum stress. The latter method is called the "third point loading" method, and yields 20–35% lower values of flexural strength than the single point loading. Thus, it becomes important to state the method of measurement when giving flexural strength values. The flexural strength values

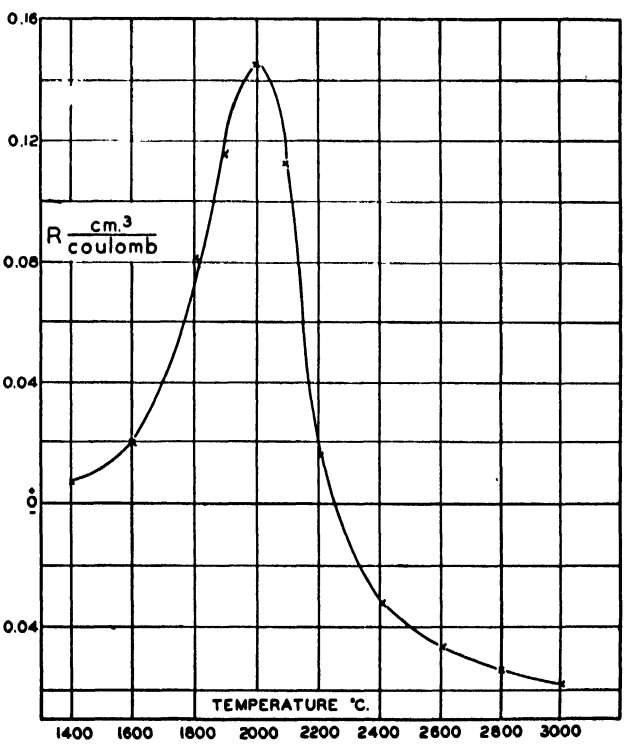


Figure 10. Hall coefficient vs firing temperature for molded graphite

given in Tables XI, XII, XIII, and XIV are for the single point loading method. The values in Table IX, however, were determined by the "third point loading" method.

A large number of measurements of tensile, crushing and single point loading flexural strengths on miscellaneous graphite samples lead to the following approximate ratios:

$$\frac{\text{Tensile strength}}{\text{Flexural strength}} = 0.53 \quad \text{(range 0.47 to 0.68)}$$

$$\frac{\text{Crushing strength}}{\text{Flexural strength}} = 2.07 \quad \text{(range 1.61 to 2.90)}$$

The crushing-to-flexural strength ratio is generally higher if the measurements are made perpendicular to the grain. In fact, the crushing strengths are nearly always greater when measured parallel to the grain. The above ratios are, of course, higher when the flexural strength is measured by the third point loading method.

A most unusual property of graphite is its increase of strength at high temperatures. Crushing strength measurements made at 1600°C indicate an increase of from 15–24% over room temperature values. Malmstrom, Keen and Green[43] have reported extensive tensile tests showing that the strength of graphite increases up to a temperature of 2500°C. At this temperature, the strength for short-time loads is 50% to more than 100% higher than the room temperature values.

The same authors were also able to measure creep in graphite at the highest temperatures, where the graphite is ductile enough to give a 7% elongation before rupture. The creep rate was measurable (about 0.1% elongation) in a two-hour period at 2300°C under a stress equal to about 85% of the breaking strength at room temperature. At 2700°C stresses of only a few per cent of the room temperature strength are enough to induce appreciable creep.

The low elastic modulus of graphite (comparable to rolled lead) contributes to its thermal shock resistance. Malmstrom, Keen and Green[43] have shown that the elastic modulus increases slightly with temperature, and that at 2000°C the modulus is about 40% greater than at room temperature.

The elastic modulus is usually measured by a dynamic method in which velocity of sound is determined by noting the resonant frequency of a sample of known dimensions. Adequate experimental evidence has been accumulated to show the same value is obtained by flexural or longitudinal vibrations, and that this value is nearly the same as that determined from stress-strain curves for low applied stresses.

By suitable technique, the measurement of resonant frequency can be extended to determine the internal friction or damping of the graphite. Westbrook[9] has used a method in which the sample is supported near one end on a two-pronged needle inserted in a phonograph record cutting head, and near the other end on the single needle of a phonograph pickup. The cutting head is connected to an audio-oscillator with a special vernier tuning dial; the pickup is connected to a vacuum tube voltmeter. The oscillator is tuned to the resonant frequency of the sample for flexural vibration, and the breadth of the resonance peak is determined by adjustment of the vernier tuner. The well known relation of breadth of resonance peak to damping factor leads to the values given in Table XXI for the per cent energy loss per cycle for different types of graphite.

Table XXI. Damping Factor of Graphite Per Cent Energy Loss per Cycle at 3000 Cycles/Sec

Graphite stock	*Grain orientation*	*Young's modulus 10^6 lb/in²*	*% energy loss per cycle*
Fine grained extruded petroleum coke base	par.*	1.72	1.34
Fine grained extruded petroleum coke base	perp.†	0.70	1.66
Fine grained extruded petroleum coke base	par.	1.21	1.25
Fine grained extruded petroleum coke base	perp.	0.87	1.32
Medium grained extruded petroleum coke base	par.	1.31	1.38
Medium grained extruded petroleum coke base	perp.	1.14	1.39
Coarse grained extruded petroleum coke base	par.	1.25	1.07
Molded lampblack base stock	par.	1.44	0.78
Molded lampblack base stock	par.	0.95	1.69
Gas-baked petroleum coke stock, fine grained, (not graphitized)	par.	2.17	0.65
Molded pitch-bonded graphitized natural graphite	par.	–	0.65

* par. = parallel.
† perp. = perpendicular.

The values lie in a reasonably narrow range for the normal graphites considering the wide variation of graphite types. The high value for natural graphite and the low value for the gas-baked stock are consistent with relating the damping to the softness of the stock.

Graphite is not perfectly elastic even at room temperature, but yields plastically to some extent. Figure 11 gives a typical stress-strain curve for graphite in flexure, and it can be seen that the deflection does not increase linearly with applied stress. In obtaining the data for Fig. 11, the stress was removed after each increase of stress and the permanent deformation was noted; this value is plotted at the left of the curve as "residual strain." Many such measurements of stress-strain curves for graphite have been made[9] both in tension and in flexure, and it is apparent that plastic flow occurs under even moderate stresses. When the stress is plotted against strain on a logarithmic scale, a linear curve is found with a slope of about 0.90 ± 0.02 up to about 30% of the ultimate strength. For greater stresses, the strain increases at an ever-increasing rate with respect to the stress. The strain at the breaking point is from 30% to 45%

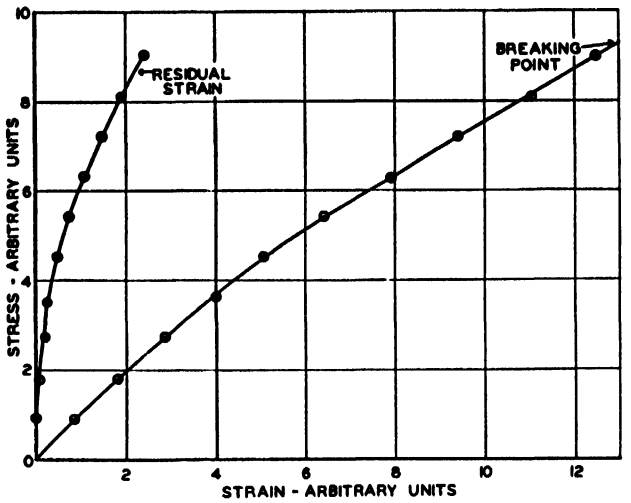


Figure 11. Typical stress-strain curve for graphite

higher than that calculated for an ideally elastic material from the ratio of the strength to the elastic modulus. Gas-baked carbon and graphitized lampblack do not exhibit this plastic deformation.

Since the real density of graphite made from petroleum coke varies from 2.18 to 2.25 and the bulk density normally varies from 1.45 to about 1.75 it is obvious that graphite has a high porosity. Reactor graphite has a porosity in the neighborhood of 25%. The sizes of the pores are naturally dependent on the grain size of the starting material and the processing steps. By using a mercury porosimeter,[44] Winslow and Glass[9] have determined the pore spectra for a large number of graphite stocks. Figure 12 gives a typical curve of the pore spectra in the range of 1 to 28 microns. The particular sample illustrated is a graphite made with a coke blend of the grain-size distribution shown in Fig. 1. As can be seen, there is an appreciable pore volume below 0.1 micron.

Since the graphite has a large volume of fine pores, it must have a fairly large surface area. A number of measurements of graphite surface area made by Glass,[9] according to the BET method, are shown in Table XXII following. It can be seen that the surface areas range from 0.47 to 0.87 m^2/gm without

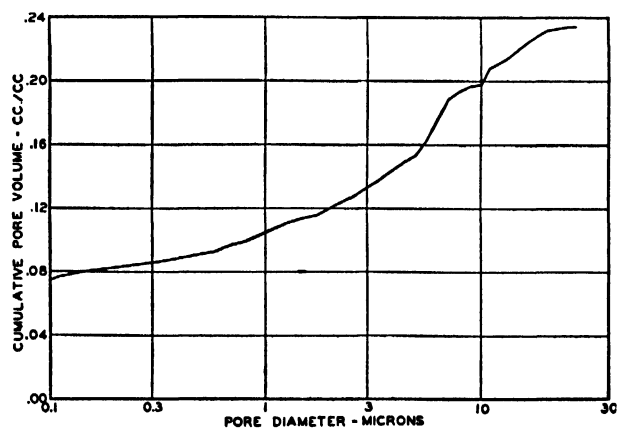


Figure 12. Pore size distribution in reactor graphite total pore volume less than indicated diameter

any apparent trend. A slow, penetrating oxidation of these graphites at low temperatures tends to open up many blind pores, exposing more surface area. For example, oxidation to a 1% weight loss increases the surface area to about 2 m^2/gm.

CHEMICAL PROPERTIES

Graphite is one of the most inert of materials with respect to chemical reaction with other elements and compounds. It is subject to only three types of attack: oxidation, formation of lamellar compounds, and reaction with and solution in carbide-forming metals in certain high-temperature ranges.

Oxidation

Graphite must be protected from oxygen at high temperatures; otherwise, it will burn to CO_2 or CO. It is interesting to note that graphite is actually less reactive to oxygen at low temperatures than many metals, but its oxide is volatile, and thus, no protective oxide film is formed. Furthermore, the high porosity of normal graphites allows penetration of oxygen and presents a rather large surface area for oxidation.

Table XXII. Surface Area of Typical Graphites

Coke source	*Maximum particle size in blend (in.)*	*Surface area (m^2/gm)*
E	Flour only	0.47
F	Flour only	0.85
E	1/32	0.61
C	1/32	0.70
C	1/16	0.69
G	1/16	0.87
H	1/16	0.58
G	1/4	0.73
H	1/4	0.80

If one defines a "threshold oxidation temperature" as that at which a sample loses approximately 1% of its weight in 24 hours, pure graphite has a threshold oxidation temperature of 520°C to 560°C depending on coke source and processing variables. Small amounts of catalysts are very effective in increasing the oxidation rate at low temperature, and there are enough of these catalysts in commercial graphite to lower the threshold oxidation temperature by as much as 100°C. Tests of individual catalysts as additives to the graphite have shown, for example, that 20 to 40 parts per million of sodium, potassium, vanadium or copper will increase the rate of oxidation by a factor of six at 550°C, reducing the time for a 5% oxidation from 120 to 20 hours.

In the temperature range 200°C to 250°C above the threshold oxidation temperature, the oxidation is still penetrative in character, such that the weight loss is greater than the volume loss. At still higher temperatures, the oxidation is diffusion-controlled, with virtually all oxidation taking place at the outside surface. In this diffusion-controlled temperature region, and to some extent in the intermediate temperature region, the oxidation rate is extremely sensitive to the velocity of air movement over the sur-

face.[45] The measurements of oxidation reported here are in stagnant air, subject only to natural convection in a confined volume.

Gulbransen and Andrew[46] measured the oxidation of graphite from 425°C to 575°C in pure oxygen at pressures of 0.15 to 9.8 cm of mercury and found that the weight of the samples varied according to the equation $W = Kt + Ct^2$, where t is the time and K and C are constants. In this equation, K is the rate of weight loss at zero time. Gulbransen found that K varied with temperature in such a way that the activation energy was 36,700 cal/mol.

Mitchell[9] has carried out oxidation tests in air on a variety of purified graphite grades at 500°C, 600°C, and 700°C. The rate of oxidation was found to increase with time, but leveled off after the samples had undergone a weight loss of several per cent. The oxidation rates during this later period of oxidation varied with temperature in a manner consistent with an activation energy of 55,000 cal/mol, averaged for ten different graphite grades. Since this value refers to a different part of the oxidation curve, it is not inconsistent with Gulbransen's work.

To indicate the order of magnitude of oxidation rates in air, the following Table XXIII gives some of the average results of Mitchell's work on both pure and commercial graphites at 500°C, 600°C, and 700°C. Mitchell's samples were 1.25 in. diameter by 2 in. long and were suspended in a furnace from an automatic recording balance. Individual values for different graphites deviated from the indicated averages by as much as 30%.

Table XXIII. Graphite Oxidation in Air — Typical Values

Graphite sample	*Number of varieties in average*	*Oxidation temperature*	*Time for 1% weight loss (hr)*	*Time for 6% weight loss (hr)*
Pure	13	500°C	200	
Pure	13	600°C	7	25
Pure	13	700°C	0.6	1.8
Commercial	1	500°C	6	
Commercial	6	600°C	0.75	2.5
Commercial	6	700°C	0.2	0.7

Similar oxidation effects on graphite are produced by steam and carbon dioxide atmospheres. However, the threshold oxidation temperature is higher for these gases. Commercial graphite will have a threshold oxidation temperature of about 700°C in steam and 900°C in carbon dioxide.

Wet oxidation of graphite can be carried out at moderate temperature by highly oxidizing agents[47] such as a mixture of potassium dichromate and phosphoric acid or by potassium chlorate in nitric acid.

Lamellar Compounds of Graphite

Graphite has been found to form a group of compounds which have been termed "lamellar", characterized by the intrusion between the layer planes of the graphite lattice of various molecules and/or ions with accompanying increase of the distance between the layer planes. The formation of such lamellar compounds can lead to extensive destruction of a formed piece of artificial graphite and prevent the application of graphite as a containing vessel or its use as anode or cathode under conditions where such lamellar compound formation can occur. Furthermore, the formation and properties of these lamellar compounds are of considerable theoretical interest. Reviews have been published by Hofmann[47] and Riley.[48] The types of lamellar compounds of graphite which have been studied can be roughly classified as:

(*a*) Compounds of graphite and certain acids under oxidation conditions, *i.e.*, in the presence of chemical oxidants or by electrochemical oxidation (graphite as anode).

(*b*) Compounds of graphite and certain of the halogens or interhalogens.

(*c*) Compounds of graphite and certain alkali metals and possibly alkaline earth metals.

(*d*) Compounds of graphite and certain metal halides.

(*e*) A fifth class represented by graphitic oxide, tetracarbon fluoride and carbon monofluoride, can be distinguished in that, whereas these compounds are found to be lamellar by X-ray examination, the type of binding between the carbon atoms and the foreign atoms (oxygen and fluorine) is different than for the other lamellar compounds. For these materials, this binding appears to be covalent, and the layer planes are no longer aromatic, but hydroaromatic.

The most extensively studied compound of Class A is graphite bisulfate, formed by exposure of graphite to concentrated sulfuric acid in the presence of such diverse oxidizing agents as nitric acid, chromic oxide, potassium permanganate, manganese dioxide, etc., or by electrolytic oxidation.[49,50] With sufficient oxidation, the compound obtained has a blue color. By a combination of chemical, pyknometric and X-ray diffraction techniques, Hoffmann and co-workers[47,50,51] have shown that in the compound formed, the layer planes of the graphite lattice are still essentially intact and that bisulfate anions and sulfuric acid anions have penetrated between these layer planes. The highest stage of oxidation corresponds to the intercalation of a layer of bisulfate anions and sulfuric acid molecules between each carbon layer plane, with the separation of carbon layer planes (along the *c*-axis) having increased from 3.34 Å to about 8.0 Å.

The most extensively studied of the second class of lamellar compounds is the bromine-graphite compound. Rüdorff[52] found that several types of graphite combined with bromine in an atmosphere saturated at room temperature to the extent of about 8 gram atoms of bromine to 1 gram atom of graphite. A surface adsorption of the bromine on the graphite appears excluded since the maximum amount of bromine taken up was the same for very finely

divided graphite and large chips of Ceylon graphite. Rüdorff concluded that a lamellar compound was formed and from his X-ray data proposed an intercalation of bromine atoms or molecules between every *second* carbon layer plane with an increase in carbon layer plane spacing to about 7 Å at these lattice positions.

The lamellar compounds of graphite with the alkali metals were extensively studied by Fredenhagen and co-workers[53,54] and by Schleede and Wellmann.[55] If a piece of graphite is brought into contact with molten potassium metal, it is rapidly wetted and in a few seconds it swells and exfoliates and its mechanical structure is essentially destroyed. This very rapid destruction of the structure of formed graphite has been reported to take place at room temperatures in a sodium-potassium alloy liquid at this temperature.[56] Two types of compounds have been recognized, one of composition corresponding to C_8K, with a layer of potassium intercalated between *each* carbon layer plane, and another of composition corresponding to $C_{16}K$, with a layer of potassium intercalated between each *second* layer plane.

The chief representative of the fourth class of lamellar compounds is the $FeCl_3$-graphite compound extensively studied by Rüdorff and Schulz.[57] On heating graphite above 200°C in the presence of anhydrous $FeCl_3$, the graphite swells strongly and $FeCl_3$ is taken up by the graphite. Excess $FeCl_3$ is readily removed by subliming or by washing, leaving an apparently fully homogeneous reaction product.

Two structures or stages are indicated, one containing (after removal of loosely held $FeCl_3$) about 56–57% $FeCl_3$, the other about 31% $FeCl_3$, and two X-ray patterns were found, distinct from each other and from the original graphite and the $FeCl_3$. The compound with the higher $FeCl_3$ content is pictured as a typical lamellar compound with a "layer" of $FeCl_3$ molecules (itself a three-plane layer lattice) intercalated between each carbon layer plane (a first-stage compound). The compound with the lower $FeCl_3$ content is pictured as a "third-stage" compound with a "layer" of $FeCl_3$ molecules intercalated between each third carbon layer plane. The spacing between carbon layer planes with intercalated $FeCl_3$ is about 9.4Å.

Reaction with Carbide-Forming Metals

Because of its ease of machining and general high-temperature stability, graphite is now one of the most universally used mold and crucible materials for critical high-temperature applications. Its high thermal conductivity is frequently desirable in providing a quick chill, and makes possible the use of graphite dies for continuous casting processes. Graphite has been found suitable commercially for the casting or melting of copper, brass, magnesium, aluminum and high and low carbon steels.[58] It is completely inert to liquid tin and bismuth up to 1500°C.[59] In addition to these metals, the Liquid Metals Handbook[56] reports that graphite is suitable for use with antimony, zinc, gallium and mercury, and has limited corrosion resistance to aluminum, magnesium, and lead. The reported unsuitability of graphite for liquid alkali metals is due to the tendency toward lamellar compound formation, as described in the previous section.

The principle limitation to the use of graphite in metallurgy is its tendency to form carbides with many metals and to dissolve in those metals. Among the strongest carbide-forming metals are molybdenum, vanadium, silicon, chromium, nickel, titanium, zirconium, and boron. Despite the solubility of carbon in these metals, graphite has been employed successfully in melting many of them.[60] For example, in the case of titanium and zirconium, Haskell[61] describes the effects of melt temperature and time while molten on the pick-up of carbon from graphite crucibles, and Kroll and Gilbert[62] give various methods of melting to minimize carbon pick-up.

ACKNOWLEDGEMENTS

We would like to thank J. A. Krumhansl and M. Janes for helping in the preparation of certain sections of this paper. We are also indebted to many other present and past members of the National Carbon Company organization for ideas and data used and for their helpful criticism. These include: J. C. Bowman, R. W. Coltman, A. C. Downes, W. B. Dexter, J. L. Gardner, J. W. Gartland, S. W. Glass, H. V. Johnson, M. T. Jones, J. T. Meers, E. Micinski, C. V. Mitchell, C. A. Odening, H. S. Pattin, R. L. Shepard, D. E. Soule, W. A. Steiner, R. S. Stroup, V. H. Wells, R. D. Westbrook, N. M. Winslow, L. L. Winter, M. S. Wright, and D. J. Zaffarano.

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The Production of Nuclear Graphite in France

By P. Legendre,* L. Mondet,† Ph. Arrongon,‡ P. Cornuault,§ J. Gueron,¶ and H. Hering, France**

The graphite used in the construction of reactors is obtained by the usual method: a paste is made starting from oil coke and pitch; it is baked in an electrical oven and the baked product is graphitized by electrical heating.

The production of nuclear quality graphite which has been entrusted by the Commissariat à l'Energie Atomique to the Société "Péchiney" required an increase in the production of that company and new shops were built in which a high degree of mechanization makes it possible, among other advantages, to reduce accidental contamination to a minimum.

In particular, use was made of pneumatic transportation in the preparation of the crude paste.

PREPARATION OF THE CRUDE PRODUCT

The coke is crushed and suitable grain size achieved by mechanical classification and automatic weighing, the product passing by gravity from one instrument to the next. The powdered coal-tar pitch is also weighed automatically and put in the mixers with a suitable load of coke. The apparent density of the baked products varies quite rapidly once the ratio between the weights of coal-tar pitch and coke changes, so that the regularity of the initial mixture and its good homogenization by mixing are of the highest importance. The possible addition of an oil which reduces the extrusion pressure required may also have some effect on the density.

Extrusion is carried out in a 3400 ton horizontal press made by Ateliers and Chantiers de la Loire.[1] The carriage which receives the extruded product is equipped with an automatic device actuated by contact with the extruded bar, which makes it possible to cut the latter at a predetermined length. Mixing and extrusion are of necessity discontinuous operations and contact between a press load and the next was studied by adding a radioactive sodium salt to certain charges. It was thus noted that the residue from the former load forms the outer surface of the extruded product in which the new load makes a sort of central conical needle. Contact is prolonged over approximately ⅓ of the products, and it will be understood that during baking, it may constitute a weak point, particularly if the successive charges of the press are not very evenly estimated. There again we find an explanation of the texture defects which sometimes appear in the current products, with the appearance of a more or less broad circle in the center of the faces of the square cross section graphite bars.

BAKING AND GRAPHITIZATION

Each one of the ten ovens in the graphitization hall can receive a minimum load of 20 tons of crude baked products. These ovens are energized by passing alternating currents through three-phase-single phase static transformers; a compensation block makes it possible to avoid too rapid a drop in the power factor when, with the progress of graphitization, the current increases (maximum 50,000 amperes per oven) while the voltage at the terminals of the oven is reduced.

During graphitization, it is important that the rise of temperature be as uniform as possible over the whole of the oven. This requirement is quite difficult to meet. In the course of baking, the temperature is checked at various points with the help of ordinary thermocouples. This is no longer possible in graphitization when the temperature exceeds 2000°C. Some tests, which conceivably were too fast, showed that thermocouples made up of graphite and carbon black, or graphite and niobium carbide, did not provide an easy solution to the problem. An optical method may be used, but it is unwieldy, and does not appear to provide a constant check-up device.††

Thus, one is limited to thermo-electrical measurements at the beginning of the operation, and to the deductions which may be made following examination of the products once the operation is finished. At any rate, the result sought can be achieved only by a lengthy series of successive approximations. It

Original language: French.

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††We do not believe that the measure of resistivity (carried out at a later time) of standard samples of a graphite or graphite paste give, as claimed by some, a good measure of the highest temperature reached. Our experiments do show that the resistivity figure obtained is substantially dependent on the duration of heating, even above 2600°C, and beyond the time during which this temperature is prevailing in the ovens.

requires painstaking care, not only in the operation of the oven, but also in its set-up and in particular in the detailed arrangement of the coke granules which separate and surround the products, and of the carborundum-sand mixture which makes up the heat absorbing layer.

PURITY

The impurities in the coke are nearly totally eliminated under the effect of the high temperatures which prevail in a graphitization oven. However, some are fairly persistent, in particular boron, magnesium, titanium, vanadium and the rare earths. Nevertheless, a combined method of graphitization and purification by a halogenated reagent makes it possible to achieve great purity for coke of any quality, in particular as regards the boron content. Silicon, present in large amounts in the oven, and other non-volatile impurities are inevitably found in the graphite. Thus, one is free to choose cokes, not on the strength of their boron content, but according to other characteristics, and particularly to the properties which they impart to the finished products.

The graphite so produced is tested by the pile oscillation method subjected to boron estimation (chemical and spectroscopic), to a semi-quantitative spectrographic examination, and to activation analyses. Most of these tests are described in other papers from France.‡‡

A product which is typical of our current fabrication gives the following analysis:

Element	*Boron*	*Calcium*	*Hydrogen*	*Iron*	*Manganese*	*Vanadium*	*Titanium*	*Total rare earths*
Content in 10^{-6}	0.3	60	15	15	0.1	23	17	0.1

As a whole, these impurities do not add more than 0.4 millibarns to the capture cross section of carbon.§§ The nitrogen trapped in the pores then constitutes an essential impurity, since its capture cross section corresponds to approximately 0.26 mb per carbon atom.

The density of our products which is close to 1.63 in ordinary production implies a porosity of 28% in volume. We verified that 95% of these pores are open pores. The gases extracted below 1100° from graphite samples heated under vacuum following degassing under vacuum at room temperature together amount to approximately 0.15 ml per gram.

Their composition, taken from an ordinary sample, is as follows:

Gas	N_2	O_2	CO_2	CO
%	14	1.5	2.5	14
Gas	*Hydrocarbons* ¶¶		H_2	H_2O
%	3.7		55	8.1

The distribution of the impurities in the various parts of the rods and in various rods from the same oven is an extremely important indication of the degree of perfection of the fabrication process. Recently we have achieved good homogeneity of the products. There is no systematic difference of importance between the central and lateral bars or between the center of the bars and their extremities. The surface of the products is a little less pure but this "skin", a few millimeters thick, is eliminated by the machining, which for mechanical reasons, affects a greater thickness. These facts not only show that the temperature is reached in the oven, but also that the following conditions are fulfilled: (1) sufficient uniformity in temperature; (2) effective control of purity of the constituents of the oven including the coke granules; and (3) no return of impurities from the edges of the oven toward the centers.

There again, the condition for success is that the oven be set up with great care, and that its operation be closely supervised.

PHYSICAL AND MECHANICAL PROPERTIES

The density achieved is a little over 1.60; but the conditions under which very much higher values can be achieved (reaching 1.74 by direct graphitization) have been defined.

Electrical resistivity is about 800 μohm/cm.

The ultimate tensile strength, close to 2 hg/mm^2, obviously increases with the density. Young's modulus (determined by measurement of the resonance frequency of a bar of known dimensions using ultrasonic vibrations) is of the order of 8×10^{10} dyne/cm^2. The size of the crystallites along the senary plane, is approximately 500 to 1000 Å.

The linear expansion coefficients are a little lower in the direction of the extrusion (1.4×10^{-6}/°C) than at right angles to it (3.2×10^{-6}/°C). The anisotropy so revealed is comparable to that shown by the electrical resistivity.

An accurate measurement of the cycles of compression and length reduction as a function of the compressive force now has been undertaken with the help of a high precision machine designed for other purposes, especifically for the study of concrete, by Mr. Berthier of the University of Grenoble. The preliminary results obtained to date show that the cycles obtained vary quite markedly with the nature of the raw materials and the conditions of graphite preparation. A correlation between the properties and other characteristics has to be established.

‡‡The regularity of manufacture is sufficient for semi-quantitative spectroscopic boron determinations at some points chosen in advance in the sample rods to warrant prediction of the values of the cross section as given by the oscillation method.

§§In addition to the manufacture of nuclear type graphite, we have designed a production process for very high purity spectrographic electrodes, the intrinsic spectrum of which is not more charged than those of Johnson and Mathey or National Carbon.

¶¶The presence of hydrocarbons other than methane suggests that reactions between the atmospheric water vapour and graphite could take place during the slow cooling in the ovens. This subject, which is of academic interest, is mentioned here for the sake of completeness.

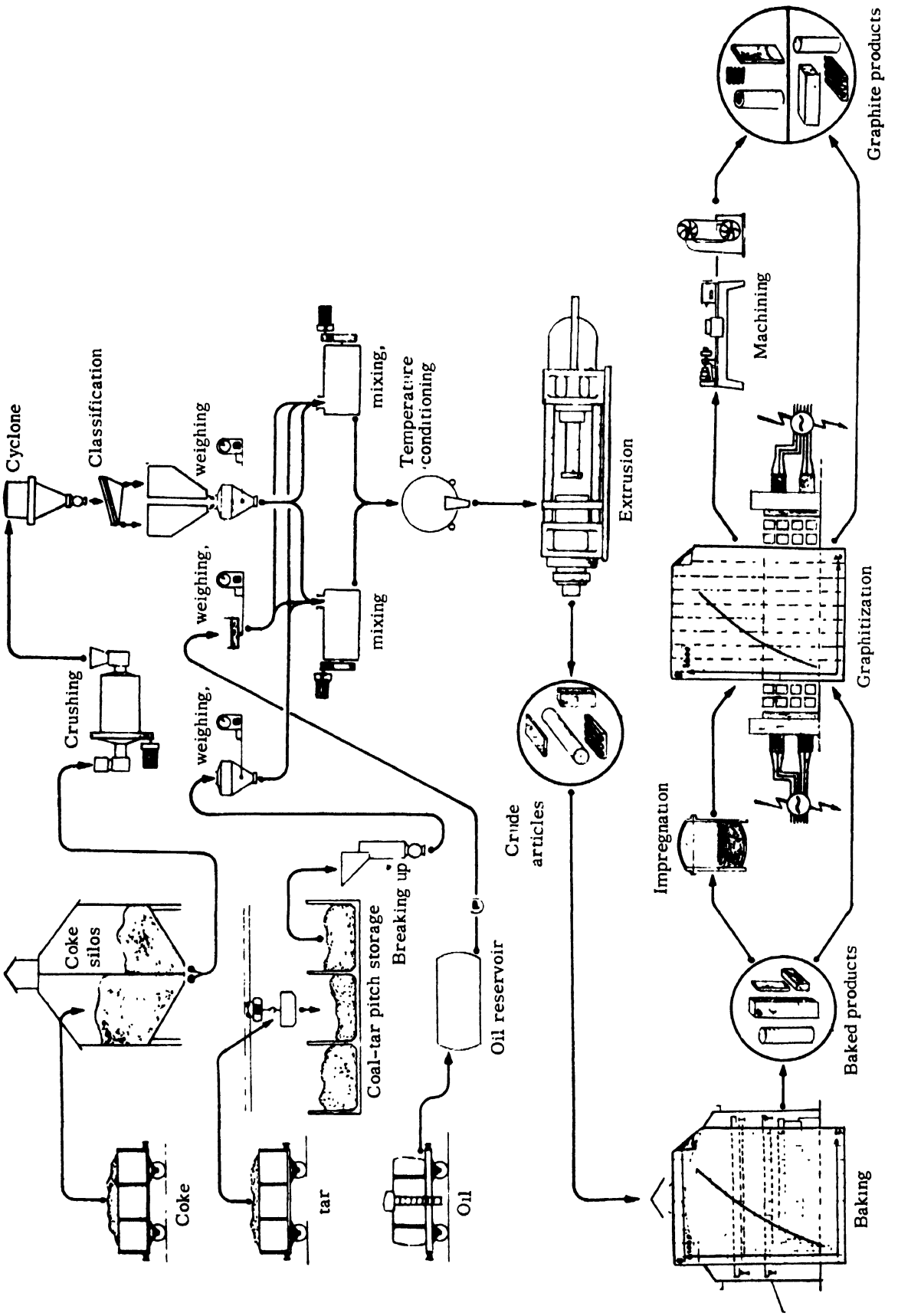

Figure 1. Diagrammatic representation of manufacturing process of artificial graphite products

MEANS OF STUDY

The laboratory of the graphitization shop where the Péchiney engineers and those of the C.E.A. work together on programs decided in common now has the following instruments at its disposal: (1) a 50 ton laboratory extrusion press; and (2) two ovens of the Tamman type with a graphite tube having an internal diameter of 100 mm and a length of 2.70 m., fed with a variable voltage of 0 to 25 v, and with currents of up to 5000 amp. The median zone presents an essentially uniform temperature over approximately 60 cm.

In addition, a pilot oven, similar to the industrial oven (but 4 m long) working under 450 kva, and capable of graphitizing 250 kg to 500 kg of produces, is located in the industrial bay. It has been used for half size experiments which proved valuable, despite the difficulties encountered when changing scales in systems having so many variables. However, the large-scale experiments are so slow (some two months between the extrusion of a rod and its coming out of the graphitization oven), that any accelerated means of study is most useful even though it might be imperfect.

From the results listed above, we shall now carry our study of the relationship between the processing conditions of graphite and its physical and mechanical qualities another step. In particular, we will look into its behavior under intense irradiation.

The methods used and the first results achieved in this field are dealt within another paper from France.[2]

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Some Experiments Concerning Pile Materials

By B. Buras,* Poland

PART 1: THE PRODUCTION OF GRAPHITE FROM LOW-BORON RAW MATERIALS†

Studies have been made of the production of pile graphite by selection of raw materials, and by raising the temperature of graphitization above the normal range in industrial practice. A second line of approach has been the production of high purity cokes by pyrolysis of certain commercially available hydrocarbons, and graphitization of the resultant cokes by conventional industrial techniques. Some work has also been done on the purification by chemical and physical means of raw materials for graphite production.

In a series of experiments on the industrial scale, the effects on product purity of selection of raw materials for low-ash, low-boron content and of raising the temperature of graphitization have been separately studied. Furnaces used for graphitizing trials were the conventional electrical resistance type having a normal charge capacity of 8–15 tons. For special trials these furnaces were sometimes loaded under capacity. Crushing, grinding, calcination, mixing with binder, pressing and pre-baking before graphitization were done in ordinary industrial equipment. In these phases no special precautions were taken to limit passage of impurities into the charges by wear of grinding, crushing or mixing surfaces, or by distillation from refractories during calcination or baking.

In preliminary work it was found that the total ash content of petroleum cokes can be halved by hand selection of the coke to reject pieces which had been next to the walls of the distilling retort. This simple procedure was used to select raw material for trials in which blocks were graphitized through a normal industrial graphitizing cycle of 72 hours in the transformer, with a charge of 2.5 tons. As a binder for these blocks, a pitch of 70°C softening point was prepared from coal tar selected for low ash content from available production in different tar-producing plants (the ash content of the tar was 0.12%). The boron and total ash contents of graphite prepared from these materials were compared with those of graphite prepared under similar conditions from non-selected petroleum coke and pitch prepared from non-selected coal tar of ash content 0.16%. The ash content of the pre-baked blocks from selected materials was on average 0.5% before graphitization, while blocks from non-selected materials had an ash content of 1.0%. The results in Table I clearly show the advantage of even such simple selection procedure in reducing boron and ash contents in the graphite.

Table I. Effect of Simple Selection of Raw Materials on Purity of Graphite

Raw materials	*Boron content of graphite*	*Total ash of graphite %*
	(ppm)	
Non-selected	10–15	0.3
Selected	2–4	0.1

Simultaneously the effect on product purity of increasing the graphitizing temperature was studied in an independent series of trials. Non-selected petroleum coke and 70°C pitch were used as raw materials. The temperature of graphitization was raised by increasing the heating time on the transformer from 72 hours to 162 hours. At the same time the charge in these furnaces was reduced from the normal weight of 10 tons to 2.2–2.5 tons, so that energy expenditure per unit weight of core could be increased for a given heating current by reduction of core cross section, and so that thicker insulating layers could be used. Results are shown in Table II.

From these results it can clearly be seen that both ash and boron contents were improved by raising the temperature of graphitization. The result with regard to total ash content is a well-known phenomenon. The result with regard to boron content is at the present moment not understood. A simple theory involving loss of boron from the charge by decomposition of boron carbide at higher temperatures is not applicable for two reasons. In the first place the temperature of decomposition of boron carbide is too high for this phenomenon to be significant in these furnaces. In the second place experiments show that an atmosphere of diffusing boron exists in the charge during at least part of the graphitizing cycle. Even if some thermal decomposition of boron carbide had occurred, then after the furnace was disconnected from the transformer the diffusing boron might tend to be fixed as carbide in the charge as the temperature of the latter fell

*The work was done on behalf of the Polish Academy of Sciences.

† Report on work done by K. Nowak *et al.*, B. Kalinowski *et al.*, S. Suknarowski *et al.*, A. Grossman and J. Landkowski.

Table II. Effect of Raising Graphitizing Temperature on Boron and Total Ash Contents of Product

Exp. no.	Charge in metric tons	Time on transformer (hr)	kwh × 10^3	Boron content of graphite (ppm) (centres of blocks)	Average ash content of (centres of graphite (%) blocks)
1.	10	72 (normal)	–	10 – 12	0.30
2.	2.5	101	99	10	0.25
3.	2.3	102	89	10	0.29
4.	2.2	162	132	2.5 – 5.0	0.08
5.	2.2	234*	–	1.8 – 3.5	0.09

*Graphitized twice; once for 72 hours in experiment 1, and again for 162 hours in experiment 4.

through the range in which boron carbide formation occurs.

The existence of a diffusing atmosphere of boron in the charge during the graphitizing cycle was shown by placing blocks of pressed highly pure coke from naphthalene pyrolysis in a graphite crucible and locating the crucible in the charge of a normally loaded graphitizing furnace. Before exposure in the furnace the coke had less than 0.5 ppm boron, and after exposure more than 5 ppm.

The diffusion of boron during the graphitizing cycle was also shown by finding that pre-baked blocks immediately before graphitization in the experiments 1, 2 and 3 of Table II, had less boron (2–3 ppm) than after graphitization (10–12 ppm). Possibly the mechanism suggested above of fixation of boron as boron carbide in the cooling core plays a part in this concentration of boron in the central regions of the furnace. This interesting phenomenon, and the observed reduction of boron in the product by raising the temperature of graphitization are under further study. Perhaps the effect of prolonging the heating time in reducing boron content lies not so much in raising the temperature of the core, but in giving more time to the diffusing boron to escape from the central parts of the furnace.

As a result of the above empirical findings, both selection of raw materials and raising the temperature of graphitization have been introduced into later work on producing pile graphite. To limit the concentration of boron from the periphery of the centre of the furnace, steps have been taken to reduce amounts of boron in the outer furnace layers as well as in the core. Fireclay bricks used in construction of normal graphitizing furnaces were found to be surprisingly rich in boron and have been replaced by a magnesite refractory of much lower boron content. Sawdust is being eliminated in the insulating coke layer. In the experiments reported above, calcined non-selected petroleum coke was used for the outer insulating layers, but in current work coke selected for lower boron content is being used. In addition for the outer insulating layers the possibility is being explored of using a mixture of carbon black and pitch, pressed into blocks, baked and broken up into suitable lump size. Carbon blacks of less than 0.5 ppm boron content are available in large amounts from native production. Production of low-boron pitch is referred to later. Carbon black/pitch mixtures do not themselves graphitize well of course, but they may give suitable low-boron, low-ash insulating material.

An approach to the problem of producing especially pure graphite has been the use of cokes prepared by the pyrolysis of naphthalene. Naphthalene was selected as being available in large amounts, and because naphthalene chars should theoretically be excellent material for graphitization.

In earlier laboratory experiments the coking of naphthalene vapour was studied in quartz, carbon, and fire-resistant steel tubes. Parameters of the coking process were evaluated to allow projection of semi-technical equipment.

During the pyrolysis of naphthalene in the temperature range 850–1200°C, three products appear: a hard coke clinging to walls of the pyrolysis tube, a powdery coke found in the pyrolysis tube, and a fine dust which is carried out of the pyrolysis tube by the stream of gases.

At 1000°C naphthalene vapour deposits a hard fine-structured coke on the walls of quartz or steel tubes. After grinding, binding with minimal amounts of 70°C coal-tar pitch, pre-baking and graphitization in a normally heated industrial graphitizing furnace, this coke was found by X-ray analysis to graphitize only to approximately 50%. When naphthalene vapour is pyrolyzed at 1200°C, the resultant coke, in admixture with 70°C pitch, graphitizes excellently in industrial furnaces, X-ray analysis showing 90–95% graphitization.

In Table III the hydrogen content of naphthalene coke is shown as a function of temperature.

The dust-like material, when obtained at 1200°C, and then submitted to graphitization in an industrial furnace, after binding with minimal amounts of 70°C pitch, was found to graphitize to only 25%, and must thus be considered as a loss from the point of view of graphitizable product.

In Table IV are shown yields of the various coke fractions as a function of temperature for a throughput of 1.65 gm/min in 20-mm diameter quartz tubes.

In laboratory studies it was determined that both commercial pressed and sublimed naphthalenes when pyrolysed in quartz tubes gave cokes containing less than 0.2 ppm boron, and ash less than 0.01%. Coking in tubes made from Polish-produced fire-resistant steel, gave no increase in boron content in the coke,

Table III. Hydrogen Content of Naphthalene Coke as a Function of Pyrolysis Temperature

Temperature °C	Hydrogen content % Hard coke	Powder coke	Light dust
850	1.17	1.50	1.63
900	1.01	1.15	1.45
950	0.76	0.95	1.35
1000	0.69	0.89	1.26
1100	0.43	0.66	0.76
1200	0.29	0.40	0.54

Table IV. Yield of Naphthalene Coke Fractions as a Function of Pyrolysis Temperature

Temp. °C	Total yield of coke %	Non-pyrolysed Naphthalene %	Losses %	Distribution of Coke: Hard coke as % total coke	Powdery coke as % total coke	Dust-like coke as % total coke
850	43.8	49.9	6.3	18.5	14.5	10.8
900	52.0	42.0	6.0	29.1	10.2	12.7
950	75.2	18.8	6.0	50.2	12.0	13.0
1000	79.6	14.4	6.0	56.0	10.0	13.6
1100	94.1	0.2	5 7	72.1	11.2	10.3
1200	94.0	0.2	5.8	68.0	14.0	12.0

although small amounts of iron passed into the product. This contamination with iron was not serious, since the total amount of contamination was within tolerance, and in any case previous studies had shown that a considerable amount of the iron present in coke can be evaporated during the graphitizing process. The carbonization of the steel tubes under the coke layer even at 1200°C was sufficiently small in laboratory experiments to warrant building the small drum-type reactor referred to later. Coking in tubes made from a baked mixture of crushed petroleum coke and 70°C pitch, did not give rise to any contamination of the naphthalene coke with boron, even at 1200°C, despite the fact that these tubes contained more than 5 ppm of boron. Such tubes can thus be used in the vertical fluidized-bed reactor for coking naphthalene described later.

Two types of semi-technical scale apparatus have been built for producing coke from naphthalene.

The first apparatus is a drum-type reactor, in which naphthalene vapour is squirted through nozzles into a fire-resistant steel coking-drum heated to 1200°C by external natural gas burners. A scheme of the reactor is shown in Fig. 1. A rectangular drum is used and coke is removed by opening the asbestos-gasket-sealed lid of the drum after allowing to cool. Progress of the coking can be followed by metering the hydrogen output. Nitrogen is used as carrier for the naphthalene vapour. Non-pyrolysed naphthalene can be recovered from the cyclone and scrubbers.

The second apparatus is designed to overcome the disadvantages of batch operation in the drum reactor. A vertical shaft of baked carbon or graphite holds a bed of naphthalene coke, fluidized in an upward gas stream. A drawing is shown in Fig. 2. Naphthalene is regularly fed to the melter. The molten output at 120°C flows to the boiler, where a constant depth of 5 cm of molten naphthalene is maintained. The vapour is pre-heated to 350°C and passes to the base of the coking shaft. Coking of the vapour occurs at 1200°C on the surface of the fluidized coke granules. As the size of the coke granules in the shaft increases, so they fall to the bottom and are removed. If pressure in the naphthalene boiler falls below 200-mm water, then nitrogen automatically flows in from the gas-holder to prevent intake of air to the coking shaft. On the basis of earlier experiments, coking efficiency is about 60–65%. The graphite or baked carbon shaft is heated externally by combustion of coke-oven gas, and is protected from burning by an outer casing of fireclay refractory.

Table V. Sieve Analysis of Pyrolysate of Naphthalene Vapour on Fluidized Coke Bed at 1200°C

Grain size (mm)	% in product
2	0.86
1.5 – 2.0	0.96
1.0 – 1.5	2.29
0.5 – 1.0	11.57
0.3 – 0.5	27.16
0.3	56.89
	99.73

Experiments on the pyrolysis of naphthalene vapour on fluidized coke beds have shown that the distribution of grain size in Table V can be obtained in the product. This grain distribution adequately meets the requirement for granularity of coke in manufacture of a number of types of graphite so that for many purposes contamination of the coke from wear of grinding surfaces in subsequent milling may be avoided.

Naphthalene coke prepared by this means is found to have low hygroscopicity, the water content after

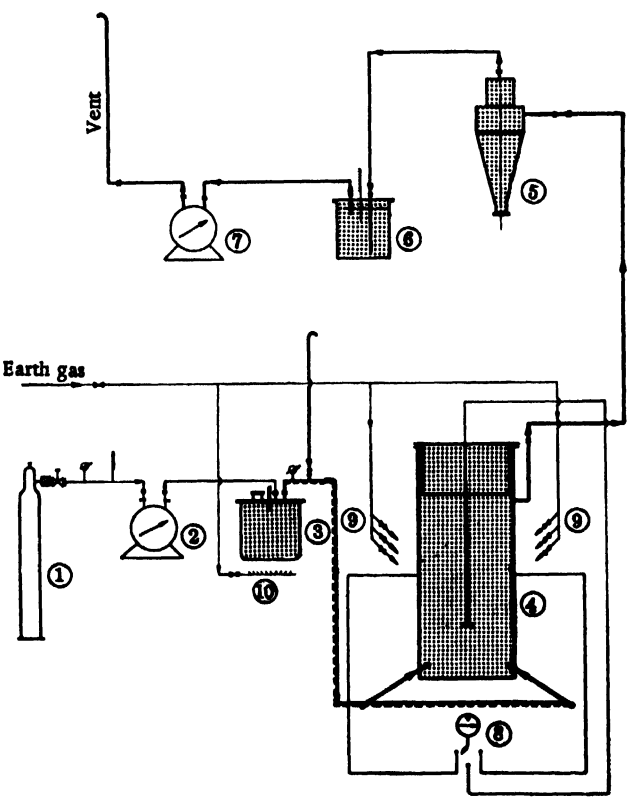

Figure 1. Drum type reactor for coking naphthalene: (1) nitrogen tank; (2) flowmeter for nitrogen; (3) naphthalene boiler; (4) drum reactor; (5) cyclone; (6) scrubber; (7) flowmeter for waste gases; (8) thermocouple recorder; (9) natural gas burners; (10) natural gas burners

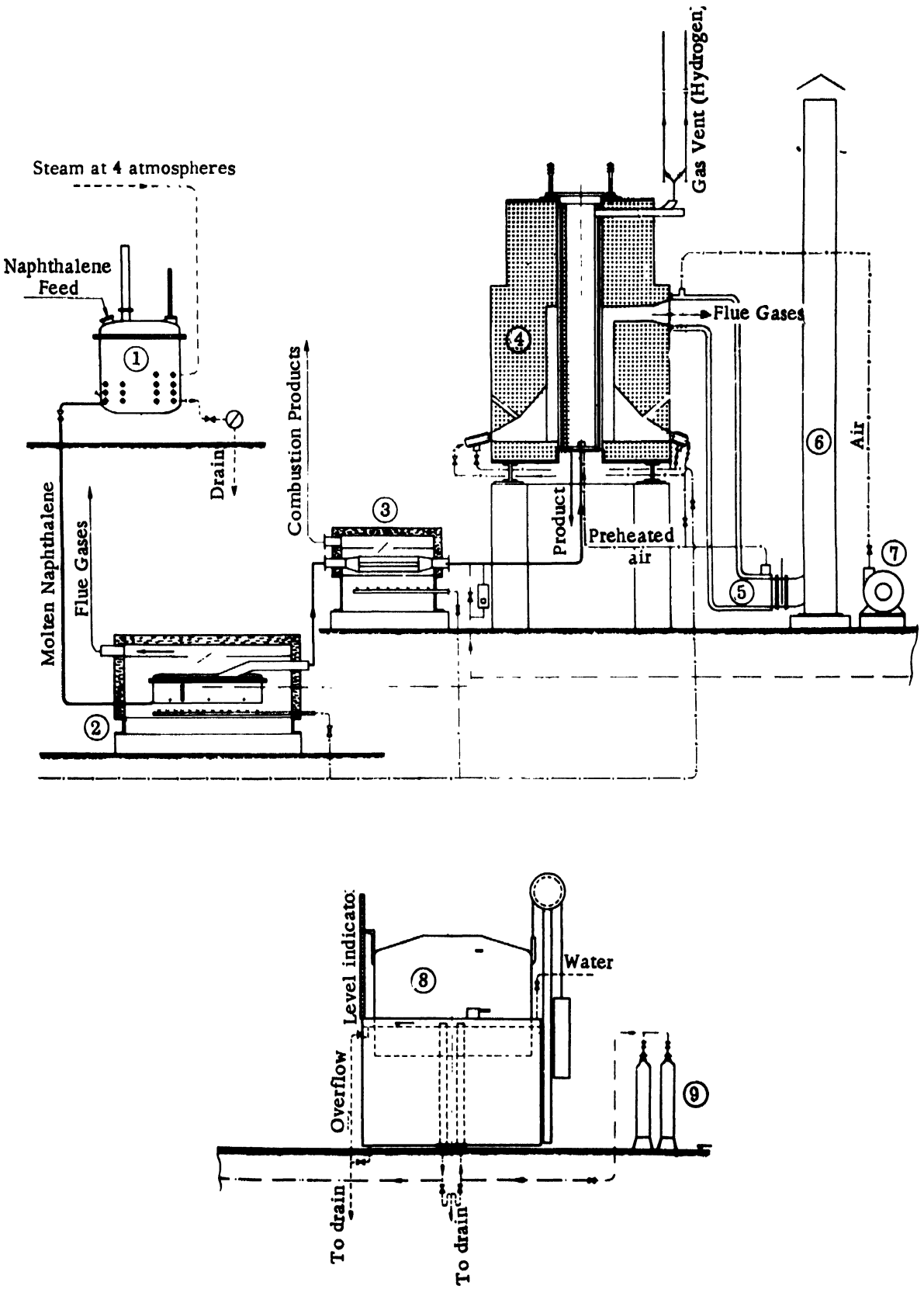

Figure 2. Fluidized bed continuous reactor for coking naphthalene: (1) naphthalene melter; (2) naphthalene boiler; (3) naphthalene preheater (4) vertical fluidized bed coking shaft; (5) heat exchanger; (6) waste gas vent; (7) blower; (8) nitrogen gas holder connected to naphthalene boiler and preheated naphthalene line; (9) nitrogen tank

Table VI. De-Ashing of Tar and Pitch by Filtration after Dilution with Benzene and Acetone

Raw material	Ash content of raw material (%)	Solvent used for dilution	% Insolubles remaining on filter	% Ash in filtrate after solvent removal
Coke oven tar	0.15	Acetone	17.2	0.014
Coke oven tar	0.15	Benzene	10.0	0.001
Coke oven pitch	0.10	Acetone	57.1	0.064
Coke oven pitch	0.10	Benzene	31.0	0.023

exposure to the open air for several days being only 0.01%. Thus special precautions during storage and transport are not necessary.

A simple horizontal graphite or carbon-tube coking apparatus is under construction for studies of coking of naphthalene and other hydrocarbons. The tube is encased in a protective refractory sheath and is heated from outside by gas burners. In such apparatus the coke deposits at the input end of the heated zone, so that in order to avoid blocking of the tube the heated zone is moved slowly along by serial ignition and extinction of a row of burners. A serious problem in such simple tube reactors is removal of the coke which clings very firmly to the tube. The reactor will be used to examine this problem and the problem of rate of hot zone transfer.

An apparatus for coking natural gas is also under construction, consisting of graphite or baked carbon rod, supported centrally in a cylinder of graphite by insulating end pieces. The central rod is heated by passage of electric current. A stream of natural gas passes through the annulus between cylinder and rod. The rod is demountable for removal of the coke formed on it. No experience is yet available with this reactor. The coke will be examined for applicability as a low-boron, low-ash raw material for graphite production.

PART 2: THE PURIFICATION OF COAL PRODUCTS FOR GRAPHITE MANUFACTURE, AND ANALYTICAL PROBLEMS‡

Work has been done on the cleaning of raw materials for graphite production by physical and chemical methods.

An economically attractive possibility is the cleaning of coal tar to reduce the ash and boron content and then to use the cleaned tar to produce coke as raw material for graphite production. Apart from this a low-boron low-ash tar is needed to produce a clean 70°C pitch as binder for production of graphite blocks.

The first approach to cleaning coal tar was to dilute the tar with readily available industrial solvents benzene and acetone, and to separate the ash by filtration, sedimentation or centrifugation of the diluted tar. The solvent is then distilled off and recovered.

Filtration is very effective in de-ashing tar, as shown by the typical results in Table VI. For these experiments dilution was in the ratio of 10 litres solvent to 1 kg tar or pitch. Refluxing was followed by filtration through "Spezialpapierfabrik" VEB hard filter No. 388. Benzene clearly has the advantage of giving a higher yield and a cleaner product. De-ashed tars can be subsequently distilled to low-ash 70°C pitch.

Sedimentation has also been applied to remove a large part of the ash of heavy tar fractions obtained by distillation of coal in a Lurgi-type still. Typical experiments were performed with a tar fraction of following characteristics: S.G. (20°C) 1.128, benzene insolubles 1.935%, softening point (Kramer-Spilker) 35°C, yield of 70°C pitch 72.96 vol % and ash content 1.31%.

When this tar was kept for several days at 90°C, and a 50 gm portion was removed from the surface of a several litre sample, the ash content of the 50 gm skimming was 0.029%. Thus a large part of the ash is not intimately bound with the tar structure, and sedimentation is in principle a feasible procedure.

However, after standing at 90°C for a further two days, analysis of the upper ⅔ of the sample showed an ash content of 1.17%. Thus sedimentation proceeds in undiluted tar, but at an impracticably slow rate. When further samples of the same tar were diluted 1:1, 2:1 and 1:2 with benzene under reflux and allowed to stand at room temperature for 48 hours, the upper ⅔ of the samples after solvent removal had ash contents of 0.021, 0.023 and 0.028% respectively. Thus sedimentation of diluted tars is an entirely feasible procedure for de-ashing. By sedimentation of benzene-diluted Lurgi distillates followed by solvent removal and distillation, low ash 70°C pitches can be obtained.

In order to speed up the settling of the mechanical impurities of the tar a further sample of the Lurgi heavy distillate of 1.31% ash was diluted 1:2 and 1:3 with benzene under reflux and then centrifuged at 3000 rpm for 30 minutes. After solvent removal from the supernatants, ash contents of 0.011% and 0.006% respectively were obtained. Centrifugation of diluted tars in these and other experiments has been shown to be an adequate means of de-ashing.

De-ashing of tars and pitches by distillation has also been examined. The fractions distilled off in a first distillation in iron or copper retorts were distilled to pitch in a second distillation. Results are shown in Table VII.

Although adequate de-ashing procedures can be easily evolved on the basis of the results previously quoted, the position with regard to reduction of boron contents of tars and pitches is not so satisfactory. The problem is complicated by difficulties in estimating the boron content of tar and pitch, referred to later.

The dilution of tar or pitch with benzene or acetone followed by filtration through "Spezialpapierfabrik" No. 388, as described in connection with Table III, does not seem to reduce the boron content in the product. This result indicates that boron

‡Report on work done by B. Roga, L. Wnekowska *et al.*, T. Jankowska, T. Czakow, D. Shugar, and J. Landowski.

Table VII. De-Ashing of Tars and Pitches by Distillation

Raw material	Ash content of raw mater. (%)	First distillation to coke			Second distillation to pitch, % pitch (on raw material)	Softening point of pitch °C	% Ash in cleaned pitch
		% Coke	% Distil.	% Losses			
Heavy tar from Lurgi Distillation	1.50	23.3	73.3	3.4	—	—	0.009
Distillation	1.50	18.3	80.0	1.7	49.4	52	0.003
Distillation	2.40	25.0	67.4	7.6	31.6	65	0.077
Distillation	2.40	21.3	72.7	6.0	30.5	64	0.03
Coke oven tar	1.13	26.0	67.0	7.0	36.5	50	0.019
Coke oven tar	1.10	55	42.5	2.5	15	91	0.091

is not predominantly located in the more easily separable mechanical impurities in the tar. However, by further reducing the pore size of the filtering medium there is some indication that a product of relatively low boron content may be obtained. Thus when a 70°C pitch of 1.10% ash content was diluted 5 times with benzene under reflux and filtered through "Spezialpapierfabrik" No. 388, followed by filtration through a G 4 filter, the product after solvent removal has less than 0.5 ppm of boron, and 0.005% ash. These interesting but preliminary indications are being followed up.

Distillation of the first 2 fractions in Table IV did not appear to reduce the boron content. It is interesting that cokes obtained from certain distilled petroleum fractions also contain appreciable amounts of boron (3–4 ppm). Thus boron can be bound to the organic substances in such a fashion as to distill together with them.

In some cases the tar fractions cleaned by the above procedures had a boron content of about 0.5 ppm. If these tars are converted to pitches and these pitches used as binders for graphite production, then from this source about 0.5 ppm would be contributed to the graphite boron content. If a low-boron coke, such as naphthalene coke having less than 0.2 ppm boron is used as the other raw material, the graphite produced will be satisfactory for many nuclear applications. However, if such tars were to be used to produce coke as raw material for graphite production, the boron content of the graphite would be too high. Therefore, further experiments have been done to reduce the boron content of tars and pitches.

Alkali and acid washing of tars has been examined as a means of reducing the concentration of boron. The main difficulty experienced here is that emulsions are readily formed during the washing and that these emulsions can be exceedingly difficult to break.

Shaking of undiluted coal-tar with aqueous solutions of sodium hydroxide or sulphuric acid at 80°C produces very stable emulsions, which on standing for 48 hours release only about 50% of the acid or alkali. Centrifuging at 3500 rpm is not of much help. It is necessary to wash the emulsion many times with hot water to eliminate acidity or alkalinity in the washings, and the tar then contains about 20–40% of water which must be removed by distillation. Such procedures are impracticable on a large scale.

Tars diluted with benzene (1:2), after filtration to remove benzene insolubles, can, however, be satisfactorily washed with sodium hydroxide or sulphuric acid. The diluted tar releases most of the alkali or acid after standing for 48 hrs. Excess benzene must then be distilled off before further washing with water, however, since otherwise a stable emulsion is formed. If the benzene insolubles are not filtered off after dilution and before washing with acid or alkali, a stable emulsion again tends to be formed.

Benzene-diluted pitches have been also successfully washed. The best way of breaking the emulsions after acid or alkaline washing of diluted pitch is to filter. As an example, a coke oven pitch of 70°C softening point was diluted 5 times with benzene and twice filtered through filter No. 388. The filtrate was then washed with 10% sodium hydroxide or 15% hydrochloric acid, or with alkali and acid successively, followed by water washing. After benzene removal a pitch of 0.007–0.014% ash content and containing less than 0.5 ppm boron was obtained. These preliminary studies indicate that acid or alkali washing of pitch diluted with benzene is a promising approach to reduction of boron content. Detailed studies of this problem are now in progress.

Studies are currently in progress on the distribution of boron in different coal fractions and on the chemical form in which the boron appears in these fractions.

The production of nuclear pure graphite raised numerous problems in connection with analytical methods.

The difficulties associated with total ash determination in low-ash tars and pitches have received attention in connection with the program described above. The majority of the published methods for ash determination depend on the careful burning of the tar in a crucible over a burner or in a muffle furnace. In some methods the whole tar is thus burned, but in other cases the lighter more volatile fractions of the tar are first distilled off and ash is then determined by burning the remainder. Such methods are of poor accuracy, which in some cases is quoted as

Table VIII. Comparison of Ash Analyses of Low-ash Tars by Flameless Combustion and Crucible Methods

Sample no.	*% Ash by crucible method*	*% Ash by flameless method*
1.	0.04	0.076
2.	0.66	1.09
3.	0.02	0.24
4.	0.10	0.26
5.	0.00	0.15
6.	0.00	0.23
7.	0.00	0.014

only ± 0.1% ash. For determination of ash contents in the low-ash tars described above, a more accurate method has been employed.

As distinct from the "extraneous" ash, the "internal" ash arising partly from the original plant material, is an integral part of the tar organic matter, and cannot be separated by some of the simple physical means described above in connection with cleaning tar. Losses of such ash during ash determination can be expected to occur if an unduly rapid rate of rise of temperature of the sample causes evaporation of a significant amount of lighter mineral-containing fractions without their combustion, or if a flame is allowed to appear on the surface of the sample leading to mechanical loss of ash. For these reasons, a gentle, flameless combustion method similar to that used in certain quantitative hydrogen and carbon analyses is preferred. Before combustion the sample is moistened with sulphuric acid of known ash content to convert cations to sulphates. Sulphates are relatively non-volatile in the combustion conditions employed, and many sulphates will be converted to oxides by the final burn out at 800°C. Some sulphate may remain in the final weighed ash, which will give a slightly higher result than an ash composed entirely of oxides. Combustion of the tar is in platinum boats in a quartz tube in a stream of carefully cleaned oxygen. Heating is by two movable electric heaters, each located initially with its nearer and 3 cm distant from the end of the platinum boat. Temperature is raised slowly to 400°C, held there for 3 hours, then slowly raised to 600°C while the heaters are steadily moved in to a distance of 1 cm from the platinum boat. For tars this state is then maintained for 2 hours, and for pitches about 1–1.5 hours. The boat then contains coke, which is burned out at 800°C to constant weight, with both heaters positioned together over the boat.

Table VIII shows that by this method higher results are obtained than with careful use of the crucible method, suggesting that distillation and mechanical losses have been significantly reduced. The present method gives more reproducible results than crucible methods, the average percentage disagreement between pairs of results for 31 pairs being 10.2% for ash content in the range 0.003–2.40%.

Spectrographic analysis of boron in graphite has been done on the ash of samples burned in oxygen at 800°C, with an excess of boron-free calcium hydroxide added to prevent boron volatilization. The ash is analysed in a Swiencicki ac arc at 15 amp on copper electrodes, using tin as an internal standard, and the line at 2497.73 Å. The tin is added to a slurry of the calcium hydroxide before the latter is mixed with the powdered graphite. Use of high quality electrolytic copper electrodes has eliminated trouble due to presence of boron in commercial carbon or graphite spectrographic electrodes.

In connection with the Polish program of chemistry for nuclear purposes, it was decided to start production of especially pure carbon and graphite spectrographic electrodes, particular attention being paid to low boron contents. Samples of electrodes from some of even the most reliable suppliers on the available world market not infrequently contain amounts of boron which are too high for certain studies.

The difficulties encountered in removing boron from already prepared electrodes are well-known. Accordingly it was decided to proceed from chars of boron-free materials, which can then be formed into electrodes in conditions which avoid boron contamination. Polyvinyl chloride and sublimed naphthalene have been pyrolysed in quartz apparatus, and used together with bakelite resin binders for graphite electrode production. Low-boron carbon black or sugar charcoals have been examined for carbon electrode production. Milling is done in agate ball-mills, extrusion in copper dies and baking in quartz muffles. Experimental lots of these electrodes show satisfactorily low boron contents.

Table IX. Purity of Hydrogen Peroxide Distilled in Jena Glass Stills

Impurity in ppm	*Crude peroxide*	*Distilled twice in apparatus 1*	*Distilled once in apparatus 2*	*Distilled twice in apparatus 2*
Dry matter at 110°C	max 2600	—	11.6	6
Free acid as H_2SO_4	max 2050	—	—	Traces
Cl^-	4.0	2.4	1.5	1
SO_4^{--}	max 3200	Not discovered	3	Not discovered
PO_4^{---}	max 1600	Not discovered	Not discovered	Not discovered
Ca^{++}	2–4	0.5	3.6	0.5
Mg^{++}	0.4	0.08	0.2	0.08
Pb^{++}	1.0	—	Not discovered	Not discovered
Fe^{+++}	0.7	—	0.13	Traces
Cd^{++}	< 0.1	< 0.1	< 0.1	< 0.1
B	—	—	< 1	< 0.5
Li	<6	<6	<6	<6

Table X. Effect on Purity of Washing Natural Fluorspar with Hydrofluoric Acid

	Impurities before washing				*Impurities after washing*		
Fluorspar	CaF_2 %	SiO_2%	Fe %	B %	SiO_2%	Fe %	B %
High grade	99.5	0.048	0.057	Traces	0.02	0.003	Not discovered spectrographically
Low grade	93.7	1.3	0.63	"	0.03	0.009	Some

As a basis for a chemical method of estimating boron in carbon products in the graphite program, the colored complex with carmine has been used, previous isolation of boron frequently being by distillation with methyl alcohol. This method has been applied to ashes from graphite burned with boron-free calcium hydroxide.

The estimation of boron in tars and pitches presents a special problem. A method has been used which involves addition of calcium hydroxide, combustion of the tar or pitch by the method previously described, followed by spectrographic estimation of boron in the ash. A significant part of the boron in these materials, however, may be bound to volatile fractions, which may be lost by evaporation during even a relatively gentle combustion. It is this doubt which has limited the statements in this report on the removal of boron from tars and pitches to the status of indications rather than conclusions.

PART 3: PURE CHEMICALS FOR URANIUM PRODUCTION§

Work has been done on the production of highly pure calcium metal needed for obtaining uranium and other metals by the calciothermic reduction of their halides. Calcium metal is obtained by the reduction of calcium oxide with aluminium powder. The metal is further purified by vacuum distillation. Selection of various available forms of the calcium oxide as raw material is being investigated to produce the most highly pure forms of the metal. In addition, work is being done on the utilization of existing deposits of natural calcites. These calcites have a very high purity and after calcination give a high yield of calcium metal in the reduction with aluminium. However the natural calcites contain sufficient lithium to give a content of about 60 ppm in the nondistilled calcium metal. Consequently it was considered worth while to examine the fractionation of calcium metal by distillation to obtain fractions with a low lithium content for high purity work, and fractions containing higher lithium content which could be used for other less exacting purposes. Condensates in the region of the condenser which has a temperature range of 475–500°C were specially examined, since this range is indicated as optimal for separation by the calcium and lithium phase diagrams. In the condenser a zone of large crystals can be differentiated from a zone of small crystals. When calcium metal with an initial lithium content 60 ppm was subjected to a first distillation, the zone of larger crystals contained 15–30 ppm lithium, while the smaller crystals contained considerably more. The larger crystal fraction when submitted to a second distillation gives a second, larger crystal fraction containing 3 ppm lithium or less. By such fractional distillation it is expected to obtain calcium containing about 3 ppm of lithium with a yield of 16–20% based on the undistilled metal.

Work has been done on the produciton of highly pure hydrogen peroxide for the precipitation of uranium tetraoxide, and other purposes. Because of the requirement to produce fairly large amounts quickly, it was decided to distill crude hydrogen peroxide obtained in existing plant by the electrolytic Löwenstein-Riedel process using ammonium persulphate, rather than set up new processes theoretically capable of giving directly a very pure product, such as the anthraquinone or silent discharge methods. It is known that during the war Merck, Darmstadt, produced highly pure hydrogen peroxide by triple distillation in glass stills.

Analyses of distilled hydrogen peroxide obtained in the present program are shown in Table IX. Apparatus was constructed from Jena Geräteglas 20, using pliable polyvinyl chloride and paraffin wax for seals, and paraffin-lined receivers. Apparatus number 1 was a simple vacuum still without rectifying column, while apparatus number 2 had a column filled with glass rings from Geräteglas 20 tubing. Yields are 95% of the peroxide. Distillation can be used to cover existing production needs.

Aluminium-plastic stills, using highly pure aluminium for still pot and column, and hardened polyvinyl chloride for condenser are also being examined for full-scale distillation.

Highly pure neutral and acid ammonium fluoride were needed for production of uranium fluorides. Ammonium fluoride production has been based on sodium silicofluoride as raw material for several reasons. Firstly this material will be available in Poland in large amounts as an industrial product. Secondly, sodium silicofluoride can relatively easily be obtained in higher purity than the natural fluorspars. The relatively high solubility of cadmium and to certain degree lithium silicofluorides offer the possibility of removing the sodium salt of these impurities by precipitation from silicofluoric acid with clean sodium chloride or soda. Further removal of boron can be expected in distillation and sublimation of ammonium fluoride. Sodium silicofluoride is ammoniated to give ammonium fluoride and precipitate

§Report on work done by M. Orman *et al.*, S. Franke *et al.*, W. Augustyn *et al.*

sodium fluoride and silicic acid. In the supernatent there remains, about 0.5–0.8 gm of silica per litre. The silica can be largely removed with potassium ion. Potassium silicofluoride was found to have a solubility in the system $NH_4F \cdot HF$ considerably lower than the solubility reported in the literature, in solution of pure HF. From the ammonolysis of sodium silicofluride a solution of the following approximate composition is obtained:

300 gm NH_4F + 15 gm NH_3 + 5 gm NaF + 800 gm H_2O

In wooden vessels this solution is acidified with a salt obtained in the manufacture of fluorides in the aluminium industry and having the approximate composition: 72% NH_4HF_2; 22% NH_4F; 5% H_2O; 1.5% NaF. The resultant solution contains in gm/litre: F 200; NH_4 150; SiO_2 750; SiO_2 0.8; NaF 4; H_2O 750. To this solution is added about 10 gm per litre of potassium hydroxide or potassium fluoride. Potassium silicofluoride settles out to give a supernatent having only 0.02–0.03% SiO_2 calculated on 100% F. After filtration, the solution is rendered alkaline with ammonia in wooden vessels and heated in impregnated graphite vessels to drive off water and convert neutral ammonium fluoride to acid form. When the boiling point of approximately 220°C is reached the molten salt is poured into a graphite vessel and distilled using a graphite condenser cooled to a temperature somewhat higher than the melting point of acid ammonium fluoride (126°C).

By these means a product is obtained after careful distillation, having the following concentrations of impurities: boron less than 1 ppm; silicon 0.01–0.03%; calcium less than 100 ppm; sodium less than 80 ppm; lithium less than 6 ppm; iron about 10 ppm.

To obtain neutral ammonium fluoride from this product, it is heated in graphite vessels on which are mounted cylindrical condensers of high purity aluminium with surrounding water jackets. Ammonia is fed to the condenser at a sufficient rate to ensure neutralization of the acid vapours at the moment of their condensation. Or, the acid vapours can be condensed into mist of liquid ammonia.

Highly pure 40% hydrofluoric acid can be obtained by dissolving in water acid ammonium fluoride obtained as above in graphite vessels, and adding a stoichiometric amount of boron-free sulphuric acid. Hydrofluoric acid is distilled off in a graphite still; sulphuric acid and additional water being periodically added to control the distillate concentration.

Natural fluorspar is purified by the following process for manufacture of sintered vessels for obtaining metallic uranium. Selected fluorspar is crushed in steel roller mills, ground in steel mortars, sieved to select optimal grains on nylon sieves, and washed in hardened polyvinyl chloride vessels with 40% hydrofluoric acid. The fluorspar is filtered off and washed on hardened polyvinyl chloride filters, dried, mixed with starch as plasticizer, formed, dried and sintered by conventional techniques.

Table X shows the importance of selection of the grade of fluorite in giving a suitably clean product.

Determination of Traces of Boron in Graphite, Uranium, and Beryllium Oxide

By J. Coursier,* J. Huré† and R. Platzer,‡ France

The problem of estimating the boron present in nuclear reactor structural materials can be stated as follows: determination, within approximately 0.1 ppm, of amounts of boron running to some tenths of a ppm.

Among the methods of estimation having the required sensitivity, we chose, because of the absence of interference from hydrofluoric ions and ease of manipulation it provides, the curcumin colorimetry technique proposed by Philipson.[1]

In order to reach the concentrations indicated, it is necessary, for the cases under review, to carry out prior separation of the boron and base materials.

An attempt was made for replacing the conventional separation technique of distillation of methylboric ester, which is lengthy and diffcult on the one hand, and unreliable for the separation of small traces of boron on the other hand.

We propose, in the case of the estimation of boron in uranium and beryllium oxide to effect separation by extraction as fluoborate and tetraphenyl arsonium compound[2] and, in the case of graphite, to achieve it by means of a cation-exchange resin. Separation by an ion-exchange resin has already been mentioned[3, 4] in connection with other applications as being suitable for quantities of boron reaching several mg.

ESTIMATION OF BORON IN BERYLLIUM OXIDE AND URANIUM

It is a well known fact that most of the anions corresponding to the general formula AB_4^-, give with such cations as tetraphenyl-phosphonium, -arsonium and -stibonium, compounds which are sparingly soluble in water, but quite soluble in chloroform. We thought that it would be possible, by extracting tetraphenyl arsonium fluoborate, to achieve separation of the traces of boron contained in the beryllium oxide and metallic uranium.

We first looked for the optimal conditions of formation of BF_4^- ion in an aqueous solution (influences of the pH of the total fluoride concentration and of the kinetics) and of extraction of tetraphenyl arsonium fluoborate (time needed to reach equilibrium, influence of the concentration of the tetraphenyl arsonium chloride, and number of consecutive extractions). This study was covered in a paper to be published in *Analytica Chimica Acta.*

Dosage of Boron in Beryllium Oxide

We carried out a certain number of tests in order to develop a good method for the determination of 0.1 ppm of boron in a sample of beryllium oxide, the main points of which we now sum up:

Regardless of the quantity of boron, the maximal difference observed during spectrophotometric determinations following extraction, is 0.01 unit of optical density, which corresponds to 0.02 μg of boron. In order for 0.02 μg to correspond to 0.1 ppm, analysis must be carried out on a 200 mg BeO sample.

The calcined and sintered beryllium oxide are attacked by a solution of 7.5M ammonium bifluoride. One can dissolve a maximum of 55 to 60 mg of beryllium oxide per ml of the buffer mix. Thus, for 200 mg, one must use 4 ml of solution.

The over-all efficiency of the process of formation of the BF_4^- ion in an aqueous solution, as well as of the extraction of tetraphenyl arsonium fluoborate, increases with the total concentration of fluoride in aqueous solution, up to a 2.5M total. Beyond that value, the quantity of boron recovered from the chloroform decreases. Thus, it is necessary to dilute the 4 ml of 7.5N ammonium bifluoride to 15 ml, in order to achieve a 2M content in the final solution.

In addition, for higher fluoride concentrations, the over-all efficiency is not the same according to whether beryllium oxide is present or not, which rules out the possibility of any calibration on blanks.

Following extraction, the organic phase is dried. The residue is again dissolved in trichloroacetic acid and an alcoholic solution of curcumin, then dried in a drying oven. Following drying, fine crystalline needles of sodium trichloroacetate are obtained, but when the quantity of tetraphenyl arsonium chloride is too large, a lacquer forms instead of crystals, which is difficult to dry and often carbonizes. In order to reduce the final amount of reagent, we carried out extractions with the help of 5, 10 and 15 ml of solvent containing variable quantities of tetraphenyl arsonium chloride. The extract was washed, thereafter, with various volumes of distilled water. Only the extractions carried out with

Original language: French.

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15 ml gave satisfactory results (80–85% yield) for a starting reagent concentration = $10^{-2}M$, the extract being washed twice with 15 ml of distilled water.

In order to make sure that the impurities which may be contained in the beryllium oxide samples are not extracted or do not interfere with subsequent determinations, we carried out our tests with and without beryllium oxide, adding to the starting solution the following elements in the concentrations indicated (ppm):

Li	100	Mn(II)	20	Si	1000
Na	100	Ni(II)	20	Al	1000
K	100	Cd(II)	20	Fe(III)	500
Ca	100	Cu(II)	100	$P(PO_4)^{---}$	100
Mg	1000				

No difference up to the accuracy in the measurements was noted between the tests carried out with and without the ions mentioned above.

We offer the following technique:

Obtaining a Solution of the Beryllium Oxide

Weigh 200 mg of beryllium oxide in a 60-ml polyethylene flask. Add 5.7 gm of 7.5M ammonium bifluoride. Bring up to 70°C in double boiler, until completely disolved. Add 10 ml of distilled water, then 1 ml of distilled water, or of a solution containing a known quantity of borax. Allow the solution to stand for at least 18 hours.

Extraction of Tetraphenyl Arsonium Fluoborate

To the solution mentioned above add 15 ml of the chloroform solution of tetraphenyl arsonium chloride, and stir mechanically for 30 minutes. Centrifuge, and remove the whole of the aqueous solution with a polyethylene pipette.

Washing the Chloroform Solution

Add 15 ml of distilled water, then separate. Again, add 15 ml of distilled water, stir vigorously for 10 to 20 seconds (do not exceed 20 seconds). Centrifuge and remove the aqueous solution. The last washing is repeated a second time. Transfer the chloroform solution to a platinum dish.

Boron Determination

Add 15 drops of $0.1N$ caustic soda and one drop of phthalein to the organic phase. Dry, by placing the capsule in a heating ramp made up of a silica tube 40 cm in length, inside which there is a heating resistor (power consumed approximately 900 w).

The solid residue is treated with 1 ml of $1N$ trichloroacetic acid over a period of ten minutes. One ml of 95% alcohol is added. Then mix and dissolve, and add 1 ml of curcumin solution. Place in the drying oven, at 105 ± 1°C, for 60 ± 3 minutes. Dissolve the residue in alcohol, bring up to 25 ml, and do a colorimetry test in a 1-cm thick cell (5400 Å).

Reagents

Ammonium bifluoride $7.5M$ (427.5 gm/l). It is recommended to use ammonium bifluoride from a flask perfectly sealed with paraffin, in order not to obtain unduly high blank runs.

Borax containing 200 mg boron per liter (1.76 gm/l). The solution is prepared by accurate weighing, and diluted 200 times.

N trichloracetic acid (163 gm/l).

$0.1N$ caustic soda (4 gm/l). It is recommended to take soda pellets from a new flask.

Tetraphenyl arsonium chloride $0.01N$ (4.18 gm/l) in AR chloroform.

0.125% curcumin, in alcohol.

Characteristics

Regardless of the starting quantity of boron, the values of the optical densities read deviate by 0.01 unit of optical density about the mean value which corresponds to 0.1 ppm of per 200 mg B/BeO.

In 20% of the tests, the mixture which is dried in the oven does not redissolve in alcohol or gives erroneous results.

The over-all efficiency of the operation is 85%, meaning that only 85% of the boron initially brought in is recovered. This result holds regardless of the amount of boron, also in the presence or absence of beryllium oxide.

In order to carry out a determination, it is preferable to add known quantities of borax to certain samples, and to draw a straight line which represents the variation of the optical density as a function of the amount of boron added. This straight line must be parallel to that obtained, under the same conditions, in the absence of beryllium oxide.

A chemist can complete a maximum of 12 tests a day. We recommend, for a determination to make two tests with beryllium oxide alone, two tests adding 25μg of boron, and two tests with 0.5 μg.

Under these conditions, as little as 0.05 ppm of boron can be revealed.

Dosage of Boron in Uranium

The attack of uranium by ammonium bifluoride or hydrofluoric acid, even in the presence of oxidizing agents leads to UF_4. On the other hand, the uranium can be oxidized up to the III and IV states by hydrochloric acid, then into U(VI) by peroxide. The following procedure is suggested for obtaining the uranium in solution and for the preparation of the solution to be extracted:

Weigh 200 mg of uranium in a 60 ml flask made of polyethylene. Add 1 ml of $4N$ hydrochloric acid. Do not seal the flask tight. Once the attack is finished (about 30 minutes), add 1 ml of 15 volume peroxide. Then, add 10 ml of distilled water, followed by 1 ml of distilled water or of a solution containing a known quantity of boron. Finally, add 2.8 gm of a $7.5M$ ammonium bifluoride solution. Allow the solution to stand for at least 18 hours.

For the extraction and estimation of boron, the operating technique is the same as for BeO.

The blank runs (without uranium) are carried out in the presence of hydrochloric acid and peroxide.

The characteristics are the same as in the case of beryllium oxide.

ESTIMATION OF BORON IN GRAPHITE

The graphite samples are roasted in the presence of calcim oxide, which is used to fix the boron as calcium borate. Since the ash content of these graphites is very low, the problem of boron separation is reduced to the separation of boron from the calcium.

Contact of the solution obtained by redissolving the product of the roasting with a cation exchange resin can carry out this separation by giving, essentially, the calcium salt of the resin on the one hand, and a solution which contains boric acid on the other, as well as the acid which further serves to solubilize the residue of the roasting.

In order to effect this contact, two methods were studied: passing the solution through a fixed resin column or mixing the resin and solution in a suitable container.

Roasting of Graphite

Sample roasting (1.00 gm) is carried out in the presence of 60 mg of calcium oxide which is supplied in the form of a 5-ml solution of saccharose-lime. The roasting time is one to two hours in an electrical oven, at $825 \pm 25°C$. A small oxygen flow makes it possible to burn the graphite completely.

Ion-Exchange Resins

Use is made of a nucleo-sulfonic synthetic resin, Amberlite IR 120, analytically pure, in its acid form, completely purified from fine residues. It has a total exchange capacity of approximately 5 milliequivalent gram of cation per gram of dry resin.

Practical capacity depends among other factors, on the granulometry, the time of contact between the resin and the solution, and the nature of the contact between the resin and solution. In order to allow for these factors, we used a safety margin by dividing the value of the theoretical capacity by a factor comprised between 3 and 5.

Utilization of the resin consists of three main operations: (1) exchange of the cations in the solution against H^+ ions; (2) washing of the resin in order to recover the whole of the acids released; and (3) regeneration of the resin.

Use of the Resin in a Column

The columns used are made of silica (or boron-free glass, or of plastic). Their height is approximately 20 cm, for a diameter of 1 cm, and they contain 10 gm of resin. The rate of flow is 1.5 to 2 ml per minute.

They allow the successive passage of at least four samples to be analyzed, without requiring any regeneration of the resin.

Passing of the Solution through the Resin

The residue from burning is redissolved in 2 ml of a solution of 1.1*N* hydrochloric acid, which corresponds to a slight excess (about 3%).

The calcium chloride solution is transferred to the resin column. Following passage, the resin is rinsed with 50 to 60 ml of distilled water, using the same rate of flow (1.5 to 2 ml per minute). The solution is recovered in a platinum evaporating dish.

Neutralization of the Solution

For 15 minutes, nitrogen is bubbled through in order to eliminate dissolved carbon dioxide which makes it difficult to neutralize the solution exactly. This is done in the presence of phenolphthalein, by 2 ml of 1.0*N* soda and a few drops of 0.1*N* soda. Very exactly 15 drops of 0.1*N* soda are then added.

Evaporation

This is carried out using a silica radiator (900 to 1000 w). At the end of the evaporation, the solution becomes saturated with sodium chloride, which deposits.

It is essential to spread out the salt on the edges of the dish, in order to make colorimetry possible: the operation is carried out by rotating the dish outside the radiator at the moment the solution begins to be saturated. As it dries up, the solution leaves an even deposit on the surface of the dish, which is not very thick.

The dry residue is then ready for curcumin colorimetry according to the technique described before.

The presence of sodium chloride (2 gm) is no problem, but the alcoholic solution requires filtering before colorimetry.

Regeneration

This is carried out once the resin is saturated with calcium. Approximately 100 ml of 3*N* hydrochloric acid are passed through and rinsed with distilled water (approximaely 100 ml) until chlorine ions are eliminated (silver nitrate check). The rate of flow is 2 ml per minute.

Duration of Operations

The total duration of separation is approximately two and a half hours. An operator can watch six columns simultaneously without any difficulty.

Reagents

Hydrochloric acid: 1.1*N* solution, as estimated, and 3*N* solution (aprox.).

Soda: 1.1*N* solution, and 0.1*N* solution.

Distilled water.

Phenolphthalein.

IR 120 Amberlite, analytical quality, acid form, no powdered residue.

Nitrogen.

Experimental Results

(Observation: the second decimal point is not significant.)

(*a*) Column blanks. A calcium chloride solution is passed through four resin columns. We find, in micrograms of boron:

Column 1 :	0.10	0.14	0.14	0.12	0.06
Column 2 :	0.08	0.13	0.08	0.14	0.08
Column 3 :	0.13	0.10	0.06	0.10	0.07
Column 4 :	0.13	0.10	0.14	0.13	0.07

(*b*) Solutions containing known quantities of boron. We passed a solution of calcium chloride which contained known quantities of boron (in micrograms):

Boron added:	0.26	0.3	0.5	0.5	0.5	0.5	0.5	0.6
Boron recovered:	0.33	0.37	0.55	0.63	0.54	0.52	0.50	1.04
Boron added:	0.6	0.7	0.7	0.7	0.7	0.7	1.0	1.0
Boron recovered:	0.62	0.58	0.50	0.54	0.70	0.50	1.14	1.09
Boron added:	1.0	1.0	1.0	1.0	1.00	1.0	1.0	1.0
Boron recovered:	1.38	0.97	0.98	1.13	0.91	1.0	1.12	0.97

(*c*) Estimation of a graphite. (Amounts of boron found in micrograms):

0.72	0.39	0.48	0.76	0.62	0.76	0.47	0.48
0.70	0.52	0.45	0.45	0.44	0.47	0.47	0.56

namely a mean value of 0.54 ±0.08 μg.

Use of the Resin in Dishes

The roasted residue is dissolved in a few ml of distilled water. Approximately 2 gm of resin, in the acid form, are placed in the dish: it has been shown experimentally that the solubility of the hydroxide and calcium carbonate in water are adequate for all the calcium to be fixed in less than a half-hour. The solution, to all practical purposes, contains nothing other than the boric and carbonic acids (the latter is eliminated by nitrogen bubbling).

This method offers the following advantages over the one described before it:

1. It needs, for separation, no equipment other than that usually found in the laboratory. The number of analyses carried out depends only on the number of operators.

2. It is less lengthy, since the preparation of columns, transfers and rinses is ruled out.

3. It is less difficult to carry out, for the absence of sodium chloride eliminates control of the evaporation and filtration of the alcoholic solution before colorimetry.

4. Finally, regeneration may be made on sizable quantities of resin at a time.

Resin Containers

The residue of roasting is carefully dispersed in a few ml of distilled water, with the help of a stirrer. Then, approximately 2 gm of resin are added, and shaken from time to time until complete disappearance of the very last traces of lime.

Rinse

The resin-solution separation is carried out, either by filtration (filter paper *boron free,* or sintered silica), or more simply by decantation (then the resin must be very painstakingly stripped of any fine powdered residues). The resin is rinsed with approximately 50 ml of distilled water added in small fractions.

Neutralization and Evaporation

Carbonic acid is eliminated by bubbling with nitrogen (bubble by bubble—15 minutes) and the solution is neutralized in the presence of phthalein by 1 to 3 drops of 0.1*N* soda (a larger number of drops indicates incomplete elimination of the carbonic gas). An excess of 15 drops of 0.1*N* soda is added, and thie solution is evaporated under a radiator. The dry residue then is ready for curcumin colorimetry, according to the technique previously described.

Regeneration

This is carried out with 3*N* hydrochloric acid, after which rinsing is carried on until the complete elimination of the chlorine ions (verification with silver nitrate).

Duration

The total duration of separation was approximately 2 hours. An operator can make from 6 to 10 estimations simultaneously.

Reagents

Hydrochloric acid: 3*N* solution, approximately.
Soda: 0.1*N* solution.
Distilled water.
Phenolphthalein.
1R 120 Amberlite, analytical quality, acid form, no fine powdered residues.
Nitrogen.

Experimental Results

(Observation: the second decimal point is not significant.)

(*a*) Resin blanks. The 2 gm of resin are left in contact with distilled water in which the boron is being determined. We found (in micrograms): 0.09, 0.08, 0.05, 0.03, 0.07, 0.1, 0.8, 1.1.

(*b*) Solution containing known quantities of boron. 60 mg of calcium oxide were roasted in an oven at 825°C (added in the form of a saccharose-lime solution) with known quantities of boron. We found, in micrograms, after deduction of the calcium oxide blanks (0.10 μg) and resin blanks:

Boron added:	0.5	0.5	0.5	1.0	1.0	1.0	
Boron recovered:	0.47	0.45	0.50	0.97	0.81	0.91	
Boron added	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Boron recovered:	0.93	0.98	1.0	1.04	0.96	1.03	1.06

(*c*) Determination in three graphites. Quantity of boron found (in micrograms):

Graphite No. 1:	0.35	0.32	0.35	0.5	0.5		
Graphite No. 2:	1.1	0.70	0.78	0.82	0.96	0.82	0.94
Graphite No. 3:	1.1	1.5	1.2	0.73	1.05	1.12	1.15

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The Correction for Instrumental Broadening of "Two-Dimensional" *hk*-X-Ray-Reflection in Carbon Black Crystallite-Size Measurements

By A. Bezjak and S. Maričić,* Yugoslavia

The manufacturing of the graphite for nuclear reactors by thermal decomposition of various gaseous hydrocarbons is described in a paper published a few years ago.[1] The graphitization process was studied by the X-ray powder technique. Recently, Schaeffer, Smith and Polley[2] have published results on carbon-black graphitization using the same experimental technique. It was of some interest to gather similar information on this subject using our domestic carbon blacks.

Among a few other characteristic changes of the X-ray diagrams in the course of the carbon-black graphitization, there is quite a definite variation in the diffusiveness of the lines. As well known, it is a consequence of the variations in the crystallite sizes. In recent years Franklin[3] has published a series of interesting reports in which important conclusions were drawn from the crystallite size measurements of various carbons before and after graphitization.

Though valuable results can be obtained by mere inspection of relative changes in the crystallite sizes, it is nevertheless desirable to know as accurate absolute values as possible. In such a case a correction for instrumental broadening of the diffraction profiles (caused by the finite dimensions of the specimen and the X-ray beam) is unavoidable.

In carbon-black graphitization studies crystallite dimension parallel to the basal-plane (001) might be of particular interest. This crystallite-dimension, often called L_a, can be determined from the width measurements of the "Two-dimensional" *hk*-diffraction lines.[4]

In the publications cited above, and in many others as well, we have not been able to find any correction-method applied to the *hk*-line width measurements. This might be explained by the fact that in many cases only relative values are sufficient; and, secondly, by the fact, that the profile of such a "two-dimensional" line is unsymmetrical as distinct from the usual "three-dimensional" lines. In a recent report Houska and Warren have applied the most general Stokes[6] method to correct *hk*-line width for experimental broadening. This method can, of course, be applied whatever the line shape may be, but is rather time consuming and unpractical in routine work.

Jones[7] elaborated a practical method for correcting instrumental line-broadening. He made some assumptions concerning the functions representing the line shapes. Shull[8] excluded any such assumption by using a Fourrier transformation technique and giving simultaneously three most common cases for the line shape equations. Berry[9] applied the same method.

In all these cases only normal, three-dimensional, i.e. symmetrical line shapes are treated. The aim of the present report is to apply Jones' idea of the instrumental broadening correction to the "two-dimensional" *hk*-reflections as occur in carbon black X-ray powder-diagrams.

EVALUATION OF THE CORRECTION-CURVE

According to Jones[7] the intensity distribution curve may be represented by

$$\psi(\xi) = \psi(0)P(\xi) = \int_{-\infty}^{\infty} g(x)h(\xi - x)dx \quad (1)$$

where $P(\xi)$ = the real distribution obtained experimentally, $g(x)$ = the function of the line-width due to the instrumental conditions, $h(x)$ = the "true" function of the line width due only to the crystallite size. If all these functions are equalized in the maximum value (= 1), then

$$B = \int_{-\infty}^{\infty} P(\xi)d\xi \quad = \text{experimentally obtained line width} \quad (2a)$$

$$b = \int_{-\infty}^{\infty} g(x)dx \quad = \text{line width due to the instrumental conditions} \quad (2b)$$

$$\beta = \int_{-\infty}^{\infty} h(x)dx \quad = \text{the "true" line width due only to the crystallite size.} \quad (2c)$$

Usually, the problem is to find $h(x)$ knowing $P(\xi)$ and $g(x)$.[6,8,9] In our case we know $h(x)$ owing to Warren's work:[4,5]

$$h(x) = P(2\theta') = K_m \frac{F^2(1 + \cos^2 2\theta)}{2\sin\theta(\sin\theta + \sin\theta_0)^{1/2}} \left(\frac{L_a}{\sqrt{\pi}\lambda}\right) F(\alpha) \quad (3)$$

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where

$$F(\alpha) = \int_{-\infty}^{\infty} e^{-(x^2-\alpha)^2} dx \qquad (4)$$

and

$$\alpha = \frac{2\sqrt{\pi} L_a}{\lambda} (\sin\theta - \sin\theta_0) \qquad (5)$$

where L_a = crystallite size parallel to the basal plane, λ = wavelength, θ = angle of the hk reflection, and θ_0 = Bragg's angle of the $hk0$ reflection.

We may put for instrumental-broadening function a Gaussian distribution, (as verified experimentally):

$$g(x) = e^{-\gamma^2 x^2} \qquad (6)$$

where x is in radians of the angle θ.

For small crystallites the intensity-range of a hk-line is very large ($\sim 5°$), but the influence of the instrumental broadening is relatively small. Thus, usual intensity corrections may be done before the correction for instrumental broadening. In the case of the larger crystallites the range of the intensity-distribution is smaller, and relative changes of the intensity-correction factor are small. In other words, it is permissible to suppose that there is practically no difference if intensity-correction is done *before* or *after* correction for instrumental broadening. We corrected the intensities always before the instrumental-broadening correction. Then,

$$h(x) = \frac{1}{1.07} F(\alpha) \equiv \phi(\alpha) \qquad (7)$$

$\phi(\alpha)$ cannot be expressed in terms of an elementary function and we replace it by an approximation:

$$\phi(\alpha) = \sum_i A_i e^{-g_i^2(\alpha - p_i)^2} \qquad (8)$$

In Table I numerical values can be found for the last approximation up to $\alpha = 5.8$, while in Fig. 1, the two functions are represented graphically.

Expressing α in radians and with the origin of the coordinate system at the maxima of $\phi(\alpha)$ ($\alpha = 0.55$), the following equation may be derived for small deviations from the origin:

$$\alpha = \frac{2\sqrt{\pi} L_a}{\lambda} \cos\theta_0 x + 0.05 = kx + 0.55 \qquad (9)$$

Table I

i	A_i	g_i	p_i	$n_i - 1$
1	0.07	2.0	−2.4	−5.4
2	1.20	0.5	0.55	0
3	−0.20	0.1	0.55	0
4	1.1	0.64	3.20	4.8
5	−0.56	1.225	3.20	4.8
6	0.60	1.21	5.60	9.15
7	−0.23	2.60	5.60	9.15

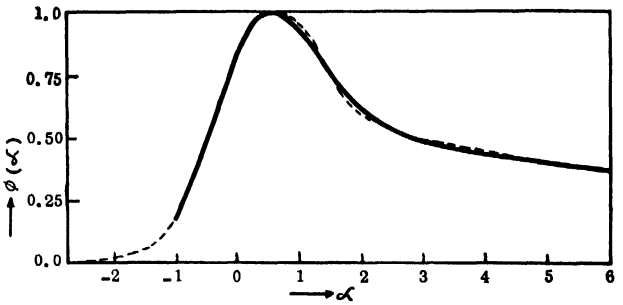

Figure 1

$$k = \frac{2\sqrt{\pi} L_a \cos\theta_0}{\lambda} \qquad (10)$$

It follows

$$\phi(\alpha) = \sum_i A_i e^{-g_i^2(kx - p_i + 0.55)^2}$$

Inserting

$$g_i^2 k^2 = \omega_i^2; \quad \frac{0.55}{k} = \Delta; \quad \frac{p_i}{0.55} = \eta_i$$

We obtain

$$\phi(\alpha) = \sum_i A_i e^{-\omega_i^2[x - (\eta_i - 1)\Delta]^2} \qquad (11)$$

where Δ is the difference between the position of the hk-diffraction maxima and the $hk0$-maxima.

The "Faltung"-theorem[10] can be used for solving Equation 1

$$\psi(\xi) = \int_{-\infty}^{\infty} g(x) H(\xi - x) dx$$

$$\int_{-\infty}^{\infty} G(t) H(t) e^{-it\xi} dt \qquad (12)$$

where $G(t)$ *and* $H(t)$ are Fourrier's transforms of the function $g(x)$ *and* $h(x)$ respectively:

$$G(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(x) e^{itx} dx \qquad (13a)$$

$$H(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} h(x) e^{itx} dx \qquad (13b)$$

Using (6) and (11) we obtain

$$G(t) = \frac{1}{\sqrt{2}\gamma} e^{-t^2/4\gamma^2} \qquad (14a)$$

$$H(t) = \sum_i \frac{1}{\sqrt{2}\omega_i} e^{-[t^2/4\omega_i^2 - (\eta_i - 1)\Delta it]} \qquad (14b)$$

Then, $\psi(\xi)$ can be expressed as

$$\psi(\xi) = \frac{\sqrt{\pi}}{\gamma}$$

$$\sum_i \frac{A_i}{\sqrt{1+g_i^2\kappa^2}}\, e^{-\frac{\omega_1^2}{1+g_i^2\kappa^2}[\xi-(\eta_i-1)\Delta]^2} \tag{15}$$

where

$$\kappa = \frac{k}{\gamma} \tag{16}$$

It follows from Equations 1 and 15 that

$$P(\xi) = \frac{\sum_i \frac{A_i}{\sqrt{1+g_i^2\kappa^2}}\, e^{-\frac{\omega_1^2}{1+g_i^2\kappa^2}[\xi-(\eta_i-1)\Delta]^2}}{\sum_i \frac{A_i}{\sqrt{1+g_i^2\kappa^2}}\, e^{-\frac{0.55\,(\eta_i-1)^2 g_i^2}{1+g_i^2\kappa^2}}} \tag{17}$$

It is convenient to use in this calculation and measurement only the small-angle side of the *hk*-diffraction lines ($\theta \leqslant \theta_{max}$). In this case, to distinguish from Equations 2*a*–2*c* it should be defined:

$$\mathrm{B} = \int_{\infty}^{0} P(\xi)\,d\xi \tag{18a}$$

$$\mathrm{b} = \int_{\infty}^{0} g(x)\,dx \tag{18b}$$

$$\beta = \int_{\infty}^{0} h(x)\,dx \tag{18c}$$

By integrating Equation 17 according to Equation 18*a* we obtain

$$B = \frac{1}{k} \times \frac{\sqrt{\pi}\sum_i \frac{A_i}{g_i}\left[\frac{1}{2} - S_{(S_i)}\right]}{\sum_i \frac{A_i}{\sqrt{1+g_i^2\kappa^2}}\, e^{-S_i^2/2}} \tag{19}$$

where

$$S_i = \frac{\sqrt{2}\, g_i\, 0.55\,(\eta_i - 1)}{\sqrt{1+g_i^2\kappa^2}} \tag{20a}$$

and

$$S_{(S_i)} = \int_0^{S_i} e^{-u^2/2}\,du \tag{20b}$$

By analogy, it follows from Equations 18*b*, *c*, 6 and 11 for b and β:

$$b = \int_{-\infty}^{0} e^{-\gamma^2 x^2}\,dx = \frac{0.885}{\gamma} \tag{21}$$

$$\beta = \int_{-\infty}^{0} \left\{ \sum_i A_i e^{-\omega_i^2[x-(\eta_i-1)\Delta]} \right\} dx = \frac{1.02}{k} \tag{22}$$

Expressing the ratios b/B and β/B we have:

$$\frac{b}{B} = 0.885\,\kappa \frac{\sqrt{\pi}\sum_i \frac{A_i}{g_i}\left[\frac{1}{2} - S_{(S_i)}\right]}{\sum_i \frac{A_i}{\sqrt{1+g_i^2\kappa^2}}\, e^{-S_i^2/2}} \tag{23}$$

$$\frac{\beta}{B} = 1.02 \frac{\sqrt{\pi}\sum_i \frac{A_i}{g_i}\left[\frac{1}{2} - S_{(S_i)}\right]}{\sum_i \frac{A_i}{\sqrt{1+g_i^2\kappa^2}}\, e^{-S_i^2/2}} \tag{24}$$

It can be easily seen from the last two equations, b/B and β/B are functions only of the parameters κ.

For graphical representation of the interdependence between b/B and β/B various values of κ should be used. As κ is becoming larger, more members of the sum Σ ought to be taken into account. In other words, the larger κ is the better approximation of the $\phi(\alpha)$ is needed. For practical purposes it is enough to calculate b/B and β/B up to $\kappa = 3$, as represented in Fig. 2. The most striking result obtained in this case is that b/B can be even larger than one, namely β/B does not equal zero if b/B is one. It is understandable if Jones' schematic explanation of his own method is connected with the fact that an *hk*-line is not symmetrical.

From Equations 10 and 22 L_a can be expressed in measureable values as

$$L_a = \frac{1.02\,\lambda}{2\sqrt{\pi}\cos\theta_0\beta} \tag{25}$$

This equation is to be used with β (in radians) after applying the correction curve from Fig. 2 for which b/B is obtained by dividing one half of the integral breadth of the standard line with the integral breadth on the low-angle side from the maxima of the examined line.

EXPERIMENTAL

There is a very safe method of testing the validity of a correction curve such as that in Fig. 2 by changing instrumental conditions.[7,9] The testing is better the larger the range of the correction curve taken into account is. Having for the time only one sort of carbon black with somewhat larger crystallites, we have been limited to vary b/B only by varying specimen dimensions and wave length of the X-radiation.

The material examined was a domestic acetylene black should have crystallites with $L_a \approx 50$Å. Though larger crystallites would be desirable for testing the range near $b/B = 1$, the dimension of 50Å is convenient because no modulating correction is needed.[5]

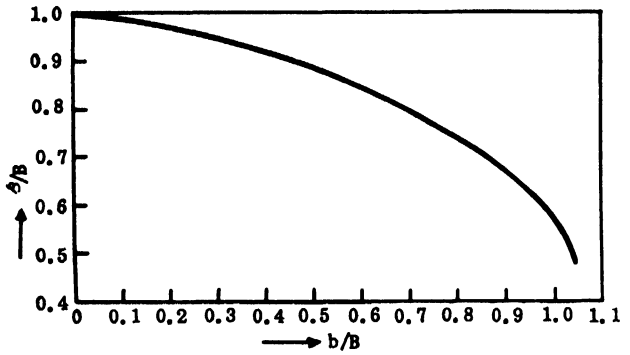

Figure 2

We have used natural good-crystallized graphite as a standard material for measuring instrumental broadening. In one case only (as indicated in Table II) it was Ceylon-graphite in flake-like form sieved through a 53 microns sieve. In all other cases a fine-powdered natural graphite from Germany (suppl. N. Branz) was used.

X-ray powder photographs were taken with 9 cm "Unicam" vacuum camera. Both the graphite and carbon black samples were extruded separately but through the same thick-walled glass capillaries without any binder. When such an extrusion was unsuccessful the sample was wetted by a few drops of xylene with no harm to the clearness of the photographs. After wetting, the paste made with a spatula ought to have proper plasticity. The extruded sample was mounted together with the capillary directly on the specimen support and centered with care, keeping the capillary out of the X-ray beam. The way described for preparing samples is essential in obtaining clear diffraction diagrams. The filtered Cu or Co K_α radiation was used.

After recording the X-ray diffraction pattern on "Ferrania" film, the diagrams were automatically photometered using "Chalonge-Lafineur"-apparatus. Microphotometer records were transmitted to relative intensities applying a graded scale where needed.

In the determination of L_a-values both the 10- and 11-line width can be generally used. There are some theoretical and practical reasons supporting the choice of 10 rather than 11 band for measurements.

The disadvantage of using this line because of some anomalies of the carbon atomic factor in this angle range, as pointed out by Franklin,[12] can be eliminated by calculating with the atomic factor according to McWeeney[13] (applied recently by Boehm and Hoffmann[14]). The double separation for this line of carbon black is negligible (Cu K_α Co K_α radiation), while the 11 line must be given a doublet correction.[5] Further, it is impossible to prepare a powder-orientation-free graphite sample.[15] The 101 line of graphite is practically free of this effect. All the others are more or less broadened by the orientation of the crystals around the capillary wall. There is no such effect with carbon black because of their sphere-like particles. (The effect is most pronounced for 001 reflection of graphite, where resolution into two lines is taking part. Consequently, graphite is useless as a standard material for L_c measurements from the 001-line width.) Finally, *if* the 11 line were taken, much longer exposure times would be required.

Table II*

Camera (cm)	*Specimen (m/m)*	*Radiation*	*Density of blackening at maxim.*	*b/B*	L_a	*Deviation from mean (Å)*
9	0.5	Cu K_α	0.255	0.37	63.8	2.8
9	0.5	Cu K_α	0.442	0.40	61.9	0.9
9	1.0	Cu K_α	0.957	0.76	58.0	3.0
9	1.0	Cu K_α	0.198	0.77	58.8	2.2
9	1.0	Co K_α	0.820	0.57	62.6	1.6

Mean value with relative standard deviation 61 Å ± 4.13%
* Ceylon graphite as standard.

There is one disadvantage in using 101-graphite reflection for measuring instrumental line-broadening, *viz.*, the existence in nearly all powdered samples of the rhombohedral modification of the graphite.[14] The rhombohedral 101 reflection is lying closely between hexagonal 100 and 101 lines. In our samples the amount of this graphite modification though not large, was just sufficient to influence seriously the low-angle side of the 101 maxima. We have used only the high angle side in measuring the integrated line width. As far as routine work is concerned one can apply a simple preliminary chemical treatment[14] of the powdered graphite to obtain clear 101 maxima.

The intensities of all 10 lines were corrected by the expression (see Equation 4):

$$\frac{F^2(1+\cos^2 2\theta)}{2\sin\theta(\sin\theta+\sin\theta_0)^{1/2}}$$

The 100 lines of graphite, when very broad (due to the specimen dimension) were given a correction for Lorentz polarization factor multiplied by F^2. In both cases, atomic factor for unsymmetrical carbon atom after McWeeney[13] was used. No correction for absorption was taken into account on the assumption that the density of the samples might be similar. Before integrating the area under the low angle side of such an intensity corrected 10 line, the maxima ought to be located with some caution. [It is advisable to compare the experimental line shape with that of $\phi(\alpha)$].

In the next table are collected all values obtained for L_a under different conditions, and calculated according to (25) using the correction curve in Fig. 2.

A measure, obtained with a specimen less than 0.3 m/m in diameter without any correction for instrumental broadening, gave the result: $L_a = 61$ Å.

CONCLUSIONS

The results from the Table II confirm the validity of the correction curve in Fig. 2. There is no general trend of the results, standard deviation being quite

satisfactory.[16] In practice, a specimen of about 0.5–0.6 m/m diameter is easily prepared, while thinner rods make difficulties. With our correction curve such specimens may be used even if b/B is exceeding 0.5, saving in this way exposure time, which can be very long for thinner specimens.

ACKNOWLEDGEMENTS

One of us (S.M.) is indebted to the Council of Education of the People's Republic of Croatia for a postgraduate scholarship.

The authors are grateful to D. Grdenić for suggesting the problem, encouragement and advice during the work.

Many thanks to Prof. Paić (Physical Institute, Faculty of Science) and S. Težak (Institute of Light Metals) for experimental facilities, and to K. Kranjc for his advice and help during the use of microphotometer. The authors also wish to thank Prof. D. Blanuša for reading the mathematical part of the manuscript of the paper.

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Production and Neutron Absorption of Nuclear Graphite

By K. Wirtz,* Federal Republic of Germany

Methods are described for the measurement of neutron absorption in relatively small quantities ($\sim$ 1.5 tons) of graphite by means of a (Ra + Be) neutron source, as well as the production and the examination of neutron absorption of pure graphite of high density ($> 2\,gm/cm^3$).

MEASUREMENT OF NEUTRON ABSORPTION

Development work on graphite gave rise to the problem of determining the absorption of thermal neutrons in relatively small quantities of graphite. A source containing ½ gm Ra + Be was available for the production of the neutrons.

The measurement of the diffusion length L has been frequently described.[1] Spherical symmetric arrangements with the source in the center would be the most favorable for measurement. However, the graphite is actually produced in rectangular blocks, out of which a cube is most frequently constructed as the simplest arrangement of high symmetry. The density distribution of thermal neutrons in this cube gives, with the help of elementary diffusion theory, the diffusion length L average over the Maxwell distribution.

At first we also studied a cube of this size which was composed of artificial industrial graphite produced by Siemens-Plania (density $\approx 1.6\,gm/cm^3$). The diffusion length obtained was $L = 40\,cm$; the transport length was $\lambda_t = 2.6\,cm$. In the case that all absorption can be attributed to carbon, the experiment yielded an absorption cross section of $\sigma_a = 7.7$ mb per C atom for a neutron velocity of 2200 m/sec. Systematic work with this graphite made it possible to reduce the dimension of the cube necessary for the measurement of the diffusion length or the absorption cross section to 90 cm; i.e., to less than $1/10$ of the quantity of graphite previously necessary. For this purpose two methods have proved feasible. In both methods the source was placed in the center of the cube, and the cube was surrounded by a layer of paraffin about 40-cm thick.

Cubicle-Surface Source

In the first case, it was possible to place between the graphite cube and the paraffin layer a cubic shell either of cadmium or aluminum 1-mm thick. The difference in the density distribution of the neutrons inside the shell with and without cadmium corresponded to the intensity distribution for a thermal source extending over the outer surface of the cube. For the evaluation of the diffusion equation

$$\Delta n - \frac{n}{L^2} = 0 \tag{1}$$

it was convenient to cover permanently the bottom and top surfaces of the cube with a cadmium layer, so that at these surfaces the neutron intensity was always zero, and to make only the four vertical surfaces into plane sources by exchanging the cadmium layers.

For the neutron distribution inside this jacket source, one can assume the following solutions for Equation 1. With the coordinate origin in the center of the cube (a = side length of the cube, including extrapolation length),

$$n = \sum_{l,\,m} A_{lm} \left(\cosh \frac{x}{L_{lm}} \cos \frac{l\pi y}{a} + \cosh \frac{y}{L_{lm}} \cos \frac{l\pi x}{a} \right) \cos \frac{m\pi z}{a} \tag{2}$$

This gives with Equation 1

$$\frac{1}{L_{lm}^2} = \frac{1}{L^2} + \frac{\bar{n}^2}{a^2}(l^2 + m^2) \tag{3}$$

For the vertical z-axis ($x = y = 0$), which runs parallel to the source surfaces, this reduces to

$$n(z) = \sum_{l,\,m} 2A_{lm} \cos \frac{m\pi z}{a} = \sum_{m} C_m \cos \frac{m\pi z}{a} \tag{4}$$

with

$$\begin{aligned} C_1 &= 2\,(A_{11} + A_{13} + A_{15} + \ldots) \\ C_3 &= 2\,(A_{31} + A_{33} + A_{35} + \ldots) \\ &\vdots \end{aligned} \tag{5}$$

or generally

$$C_i = 2 \sum_{k} A_{ik},\ i, k = 1, 3, 5 \ldots$$

For a vertical axis, which runs parallel to the z-axis ($x = y = x_0$) in the inside of the cube, the corresponding expression is

$$n(x_0, x_0, z) = \sum_{m} B_m \cos \frac{m\pi z}{a} \tag{6}$$

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with

$$B_1 = 2\left[A_{11}\cosh\frac{X_0}{L_{11}}\cos\frac{\pi X_0}{a} + A_{13}\cosh\frac{X_0}{L_{13}}\cos\frac{3\pi X_0}{a} + - - -\right]$$

$$B_3 = 2\left[A_{31}\cosh\frac{X_0}{L_{31}}\cos\frac{\pi X_0}{a} + A_{33}\cosh\frac{X_0}{L_{33}}\cos\frac{3\pi X_0}{a} + - - -\right] \quad (7)$$

or generally

$$B_i = 2\sum_k A_{ik}\cos\frac{X_0}{L_{ik}}\cos\frac{k\pi X_0}{a}$$

The convergence of the coefficients A_{ik} is in general good and was in some cases more exactly studied. Therefore, it is sufficient to use only the first two harmonics. Further, because of the cubic symmetry: $A_{ik} = A_{ki}$ and $L_{ik} = L_{ki}$.

It is sufficient to measure the density of thermal neutrons along the axis $(z, 0, 0)$ and (z, x_0, x_0). From the experimental curves $n(z)$ and $n(z, x_0, x_0)$ one obtains by a Fourier transformation of the general type

$$C_k = \frac{1}{a}\int_{-a/2}^{a/2} n(z)\cos\frac{k\pi z}{a}\,dz \quad (8)$$

the coefficients C_m and B_m. From Equation 4 there follows

$$A_{11} = \frac{C_1 - C_3}{2};\quad A_{31} = \frac{C_3}{2} \quad (9)$$

From this and Equation 7 we obtain the transcendental equation

$$\cosh\frac{X_0}{L_{11}} = \frac{1}{(C_1 - C_3)\cos^2\frac{\pi X_0}{a}}\left[B_1\cos\frac{\pi X_0}{a} - B_3\cos\frac{3\pi X_0}{a}\right] \quad (10)$$

Its solution gives the relaxation length L_{11} and also with Equation 3 the diffusion length.

Studies of this sort with artificial graphite have been made by J. Garcia Fité in the Max-Planck-Institut für Physik in Göttingen. The result for L agreed within experimental error with that measured in the large cube.

Integral Method

The second method avoids the use of diffusion theory and permits the comparison of the unknown absorption cross section of graphite with the known cross section of paraffin. This method proved to be the simplest and most reliable, and it was this method which was used for the development work on graphite of high density. First, however, it was likewise tried out with graphite of normal density, in order to obtain the relation with the aforementioned measurements.

The source was again placed in the center of the graphite cube, which was surrounded by the 40 cm paraffin layer. (The cadmium or aluminum sheets were not present). All source neutrons, Q per second, were completely absorbed inside this arrangement, part in the inner graphite cube and part in the paraffin cover. By integration of the neutron density distribution $n(x, y, z)$ over the whole graphite volume

$$N_c = \int_{Graphite} n_c\,(x, y, z)\,dx\,dy\,dz \quad (11)$$

and likewise by integration of $n_p\,(x, y, z)$ over the entire paraffin cover

$$N_p = \int_{Paraffin} n_p\,(x, y, z)\,dx\,dy\,dz \quad (12)$$

one obtains

$$Q = N_c\,\Sigma_c\,v + N_p\,\Sigma_p\,v \quad (13)$$

(v = neutron velocity; Σ = macroscopic absorption cross section). Q is obtained from the integral N_p^0 of the source neutron density in a cube of side-length of about 1.6 m which consists only of paraffin, and in which all source neutrons will be likewise absorbed.

Then

$$Q = N_p^0\,\Sigma_p\,v \quad (14)$$

From Equations 13 and 14

$$\Sigma_c = \frac{N_p^0 - N_p}{N_c}\Sigma_p \quad (15)$$

Because of the $1/v$ dependence of the absorption cross section, there is no dependence on the Maxwell distribution of the neutrons. The epithermal absorption of fast neutrons of the source during the slowing-down in the hydrogen of the paraffin makes it necessary for N_p^0 to be increased by 1%. The usual foil corrections must be considered. For the atomic absorption cross section of the paraffin a value of $\sigma_a(CH_2) = 0.665$ b for $v = 2200$ m/sec was used. The purity and chemical composition CH_2 of the paraffin was controlled analytically. In this way, for the industrial artificial graphite, $\sigma_a = 7.9$ mb was obtained, which agrees within the error of measurement with the value that corresponds to the diffusion length of the first method.

Mr. K. H. Böckhoff was chiefly responsible for this experimental work.

NATURAL GRAPHITE OF HIGH DENSITY

The production as well as the mechanical, thermal and nuclear properties of artificial graphite are well known.[2] Artificial graphite is obtained from pressed coke, mostly petroleum coke, through "graphytiza-

Table I. Neutron Absorption Cross-Section per Carbon Atom Obtained with the Integration Method in Cubes of 90 x 90 x 90 cm.

No.	*Type*	*Mean density of the cube, gm/cm³*	*For 2200 m/sec, millibarn*	*Remarks*
1	Artificial graphite from Siemens-Plania	1.57	7.9	Not produced for purposes of nuclear physics
2	Natural graphite from Kropfmühl	2.057	7.6	Still contains chlorine from the purification
3	Natural graphite from Kropfmühl	2.072	5.2	Sodium carbonate purification
4	Natural graphite from Kropfmühl	2.072	4.8	Sodium carbonate and chlorine purification; chlorine removed
5	Pure carbon	—	4.5	Table value; c.f., e.g., Hughes, Pile Neutron Research

tion" at a very high temperature. Although the density of crystalline graphite is nearly 2.3 gm/cm³, the density of the artificial graphite, which likewise consists of a network of small crystallites, seldom exceeds the value of 1.7 gm/cm³, since the density of the coke determines the density of the final product.

In southern Germany there are great deposits of graphite ores, which contain 20% graphite in the form of relatively large crystal flakes. The graphite can be extracted after crushing the rock by flotation methods. The *Graphite Factory Kropfmühl* in Munich, a producer of natural graphite, in collaboration with the Max-Planck-Institut für Physik in Göttingen, was successful in producing from this material formed graphite pieces, which were very pure as well as mechanically and thermally stable. The method of production is briefly the following:

1. The concentrated flakes, containing about 93–95% carbon, are heated to high temperatures (800–1000°C) in the presence of chlorine gas or sodium carbonate as well as catalyzers. The impurities are transformed partly into gaseous or water soluble compounds.[3] The remaining graphite contains only about 0.04% ashes, which are composed mainly of oxides of the elements Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, Cr, Ni and V. The concentration of rare earths and of boron is less than 0.1 ppm, probably much less. As a whole, these impurities should not raise the thermal absorption cross section per carbon atom more than 0.07 mb.

2. This material is finely crushed and then is compressed at high pressure (3000 kg/cm²) and normal temperature into formed pieces of density 2.05 to 2.07 gm/cm³. The pressed pieces are polished only on the surfaces that are perpendicular to the direction of pressing. The compression of the graphite is successful only with material of a certain chemical history.

3. These pieces undergo a thermal hardening at a temperature of 800°C to 900°C in a suitable gas atmosphere.

4. Finally the pieces are controlled with respect to their mechanical properties and their absorption of thermal neutrons.

Up till now only blocks of 8 × 8 × 5 cm have been produced in which the planes 8 × 8 cm were perpendicular to the direction of compression. The density of these samples was invariably around 2.06 to 2.07 gm/cm³. An arrangement of these blocks in the form of a cube of about 90 × 90 × 90 cm resulted in a mean density of the cube that was only 0.2% to 0.3% less than that of the blocks themselves.

The *limit of mechanical compression* was studied for single blocks by means of a hydraulic press with pressure being applied parallel to the original direction of compression. The steel planes of the pressure extended well over the edges of the blocks. Between the blocks and the steel surfaces were placed layers of blotting paper. Up to a pressure of 50 kg/cm², the blocks showed no change; above 50 kg/cm², there appeared small flaking at the edges; at 125 kg/cm² the blocks showed small fissures, and at 180 kg/cm² failure occurred.

The graphite can be as easily machined with a lathe as artificial graphite. In some cases it may be advisable to harden the formed pieces first after the machining; in this manner the stability of the edges of the machined areas can be improved.

The *thermal conductivity* of the blocks is about 0.3 $cal/cm^{-1}-sec^{-1}-deg^{-1}$ and thus corresponds approximately to that of artificial graphite.

The resistance to heating has been studied in a preliminary manner. In vacuum, heating over a considerable period of time to a temperature of 800°C was possible with no difficulty, and even at 1700°C there was no damage after three days. In the presence of air damage appeared at a temperature of 450°C, similar to the behavior of artificial graphite.

No experiments have been made so far concerning stability in the radiation field of a reactor, but it can be hoped that the results will be similar to those obtained for artificial graphite.

From each of three different samples of the highly purified natural graphite, two-ton blocks were produced. Their neutron absorption cross section was studied by means of the integration method. If the whole absorption is considered to be due to carbon only, the results shown in Table 1 are obtained. In this table the corresponding measurement with the artificial graphite is given. Obviously samples 3 and 4 can be considered suitable for nuclear purposes, under the assumption that our method contains no systematic error.†

From the values for σ_a given in Table 1 for $v_0 = 2200$ m/sec, the diffusion length averaged over the Maxwell distribution is obtained by means of

$$L^2 = \frac{\lambda_t}{3}\frac{1}{\Sigma_a(v)} = \frac{\lambda_t}{3}\frac{1.128}{\Sigma_a(v_0)}$$

with $\bar{v}$ = average velocity

†The error from the measurements should be less than 3%.

$$\bar{v} = \frac{\int n(v)\, v dv}{\int n(v)\, dv} = 1.128\, v_0$$

$\Sigma_a(v_0) = N\sigma_a(v_0)$; N = number of carbon atoms per cm³; and $\lambda_t = 2.6$ cm for density 1.6 gm/cm³.

For the absorption cross section $\sigma_a = 4.8$ mb of sample 4 with a density of 1.6 gm/cm³, the diffusion length $L \approx 50.4$ cm is obtained; for a density of 2.072 the length $L \approx 39.0$ cm.

ACKNOWLEDGEMENTS

I wish to thank Professor Heisenberg for help and criticism, and Graphitwerk Kropfmühl, München, especially Director K. Erhard and Mr. H. Ulrich for their kind cooperation.

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Record of Proceedings of Session 16B.2

TUESDAY AFTERNOON, 16 AUGUST 1955

Chairman: Mr. F. Giordani (Italy)

Vice-Chairman: Mr. A. Clemente (Philippines)

Scientific Secretaries: Messrs. A. Finkelstein and B. Prakash

PROGRAMME

P/534 The production and properties of graphite for reactors ..... L. M. Currie *et al.*

P/343 Production of nuclear graphite in France ..... J. Gueron *et al.*

P/943 Some experiments concerning pile materials ..... B. Buras

DISCUSSION

Mr. L. M. CURRIE (USA) presented paper P/534.

Mr. J. GUERON (France) presented paper P/343 with the following remarks:

The production of graphite for nuclear purposes in France has been carried on, since the creation of the *Commissariat á l'Energie Atomique* (Atomic Energy Commission), by the joint efforts of the *Commissariat* itself and the *Société Péchiney*. This industry has now reached a turning point, since the purification problems have been practically solved whatever the raw material may be. In the future we shall have to put ourselves in a position to supply pile engineers with a whole range of products to enable them to carry out very widely differing schemes. We must therefore learn to produce at will graphite of varying density which is resistant to radiation effects, the characteristics of which have been discussed in great detail in previous sessions. We must also refine the detailed processes of manufacture, which is in many respects still at the craftsman stage. To mention only one sympton of this, I will remind you that although we can make optically pure graphite, we cannot make graphite with physical properties that remain constant throughout a single bar without some few per cent of error. This example is enough to prove that unemployment is not yet lying in wait for graphite engineers.

Mr. B. BURAS (Poland) presented paper P/943.

DISCUSSION OF P/534, P/343 and P/943

Mr. K. WIRTZ (Germany): I want to ask Mr. Currie two questions, and I want to make one remark on this paper. The first question is: How have the low absorption cross sections of 3.2 to 3.5 been measured?

Mr. CURRIE (USA): Those were determined directly by the General Electric organization in the Hanford pile. I think that there are others present in this room this afternoon who can answer better than I, for instance, Mr. Hennig.

Mr. G. R. HENNIG (USA): We determine the absorption cross section of carbon-12 by determining the increase in carbon-13 concentration after a known flux. We determined similarly the concentration of carbon-14 which was produced by carbon-13, and thereby determined the cross section of 3.2 ± 0.2, and then in a separate determination with a pile oscillator we confirmed these cross sections.

Mr. WIRTZ (Germany): I asked my question because of the way you described it. You get a carbon cross section but not of the whole graphite.

However, if you have confirmed it by a pile oscillator, that answers my question.

Mr. HENNIG (USA): Maybe I did not understand you; but it seems to me that if the graphite contains only carbon-12 and carbon-13, then the appropriate sum of the two absorption cross sections should be the absorption cross section of carbon. This is what we confirmed by a pile-oscillator experiment.

Mr. WIRTZ (Germany): May I add this statement, that we have mechanically stable blacks pressed from natural graphite and that they have a mean absorption cross section up till now of about 4.6 millibarns and a density of 2.1. I though that might interest you.

Mr. H. HERING (France): I should like to ask Mr. Currie a number of questions:

1. Is the "GBF" purification process quoted by Woods the same as that just mentioned by Mr. Currie, or can the purification referred to by Woods be carried out in an ordinary Acheson furnace?

2. For what reasons was it decided, in the United States, to manufacture reactor graphite in sections of $4\frac{1}{2} \times 4\frac{1}{2}$ inches?

3. With regard to the effect of the particle eccentricity of coke on the behaviour of graphite under irradiation, am I right in thinking that an increase in this eccentricity increases the ratio of transversal to longitudinal expansion?

4. In your paper you state that it is possible to make graphite with densities greater than 1.90 by using furnace black, but that it is difficult, indeed

very difficult, to produce graphite of more than one inch in diameter in this way, owing to the low permeability of the products used. What form does the difficulty take? That of swelling during firing?

5. Was the lampblack stock referred to Table XI obtained in the usual manner, coke simply being replaced by lamplack? And can we assume from its high coefficient of expansion that it would expand considerably under irradiation?

6. Do you regularly measure the temperature in graphitization furnaces, or is this done only exceptionally?

Mr. CURRIE (USA): The GBF purification as mentioned by Mr. Woods is essentially the purification method we are talking about. Some of the materials may not have been identical because there have been changes in raw materials through the years, but essentially the GBF material referred to by Mr. Woods is the same as the material we are talking about here.

The answer to the second question, about the choice of sizes for cross section, of about $4\frac{1}{2} \times 4\frac{1}{2}$; it was not always that—it was in that neighborhood. That was a combination of circumstances: one was the dies available then, and the other was the design requirements for the piles then being built.

With regard to the next question about the eccentricity of the particles, I think that (for the same base stock) if you increase the eccentricity of the particles you can expect to increase the anisotropy of the graphite. The answer to your question is yes.

Regarding your question about carbon black material giving a density of 1.9, and making the material much larger than a cross section of 1 inch, this gives you a very low permeability. In the green stock it causes distortion and cracking, and as such we have not considered it really commercial: it takes too much time and care in the handling, and at present I do not think we care to go in for a much larger section of this highly filled lampblack material. The black was introduced directly into the base stock by substituting lampblack for some of the materials. It was, of course, necessary to adjust the pitch in the rest of the composition to give you the right properties. I do not know that this high dilution coefficient would mean that it would give you higher expansion on irradiation I think the data given before would indicate that. I am not sure that you can extend them for the materials of this base stock. If you were to guess, it would probably be in that direction.

Then you asked about the ways of measuring graphitizing temperatures. There are several ways. Optical measurements are not too satisfactory. For routine manufacturing runs with furnaces of the same size and with the same charge, temperature is controlled by the rate of advancing power input and that gives you a pretty steady temperature rise and temperature measurement at the end. Each furnace charge is not measured optically, but the control is very careful.

Mr. J. P. HOWE (USA): I would like to ask Mr. Guéron: What halogen compounds or halogens are used for purification, and what conditions of time and temperature are most effective?

Mr. GUERON (France): I am sorry to have to follow the example of Sir Christopher Hinton when he explained, during the session on reactors yesterday, that trade secrecy had to be brought into this Conference, and I am extremely sorry that I am unable to give a detailed reply to the question which has just been asked.

Mr. W. K. WOODS (USA): We have not previously inquired about whether you have had any experience with the radiation damage effects in graphites of various densities.

Mr. GUERON (France): We have not yet had such experience. We feel that the systematic study of the effect of radiations on graphites, in relation to their density in the case of compositions or materials of the same kind, and at a practically constant density when the nature of the materials is changed very considerably, is extremely important, so that pile-building engineers will be in a position to know precisely what range of graphites is available to them for their various schemes. I believe that you were asked this same question in a previous session, and you said that you yourselves were not altogether sure that you had meaningful data on this subject. As I said in concluding, I feel that that is now one of the questions that we all ought to try to solve, and I hope that we shall be able to do so to a large extent by combining our efforts.

Mr. CURRIE (USA): I would like to ask Mr. Buras two questions, and perhaps I can ask them consecutively. Would you care to state what the sizes of the graphite shapes were that you made from the napthalene coke? Also there is a question the answer to which I could not find in your paper: how did the chemical purification of the pitch or tar affect the physical properties of what you made from it? Did you have a change in the pitch at all?

Mr. BURAS (Poland): The sizes of graphite shapes at present in experimental production are 20 cm × 20 cm × 100 cm. With regard to the second question, purification of the pitch has not been observed to change the physical properties of products made from it

Mr. HERING (France): I find Mr. Buras' method for determining the ash content of the pitch extremely interesting. I should like to ask him what was the size of the sample used each time.

Mr. BURAS (Poland): Several grammes.

Session 17B.1

PRODUCTION TECHNOLOGY OF SPECIAL MATERIALS: ZIRCONIUM

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Zirconium Metal Production

By S. M. Shelton, E. D. Dilling, J. H. McClain,* USA

Zirconium metal and zirconium-rich alloys have excellent corrosion resistance and suitable physical properties provided interstitial impurities including carbon, nitrogen, oxygen and hydrogen are removed to low limits.

Hafnium, because of its inherently high thermal (slow-speed) neutron absorption is objectionable in reactor-grade zirconium.

Zirconium metal production on a large scale in the United States, has been tailored to meet the specifications for reactor-grade zirconium. High-hafnium zirconium with essentially the same physical and chemical properties, but much less costly to produce, has reached only the development stage.

This report describes the current status of zirconium metal production, with a detailed account of the production of reactor-grade zirconium by the Bureau of Mines.

ZIRCONIUM ORES

Zirconium formerly considered in the class of rare elements, actually is more plentiful in the earth's crust than nickel, copper lead, zinc, and some of the other familiar metals. Zircon the most widely distributed and most important source of the metal, is an orthosilicate with the formula $ZrSiO_4$ (theoretically 67.2% ZrO_2 and 32.8% SiO_2). A less important source mineral because of its restricted occurrence, is baddeleyite an oxide of zirconium.

Hafnium, the homolog of zirconium, occurs almost invariably associated with zirconium minerals; with the exception of the rare mineral thortveitite, zirconium always is present in much higher concentrations than hafnium. The hafnium oxide content of zircon and baddeleyite varies between 0.5–2.0 per cent and 0.5–1.8 per cent, respectively. Certain altered varieties of zircon, such as alvite and cyrtolite are the richest sources of hafnium and contain as much as 17 per cent hafnia.

Commercial concentrations of zircon are restricted almost entirely to beach sand and stream-placer deposits; however, minor production has been reported from operations in pegmatite dikes. Production from Florida and imports from Australia supply the zircon requirements of the United States. Relatively small quantities of baddeleyite are received from Brazil.

*US Department of the Interior, Bureau of Mines, Albany, Oregon.

Reserves of zirconium minerals in the countries of the Free World appear adequate to support any expansion in use foreseeable at this time. Reserves in the United States have been estimated between 5 and 15 million short tons. Estimates as high as 2 million tons have been reported for baddeleyite in Brazil and zircon is known to occur in substantial quantities even though no values have been assigned. Reserves of 1 million tons of zircon have been credited to Ceylon and values as high as 5 million tons have been reported for India. Zircon reserves in Australia are believed to be high but no reliable estimates are available.

Consumption of zircon in the United States, estimated between 25,000 and 30,000 tons for 1953, has been increasing steadily over the past few years. Substantial increases have occurred in the nonmetallic applications and although, at present, only a minor quantity of the mineral is being used in the production of ductile zirconium metal, the potential is large.

Table I lists world production of zircon for the period 1946–1953.

ZIRCONIUM PRODUCTION METHODS

History

The passage of over one hundred and thirty years from the discovery of zirconium by Klaproth in 1789 to the first production of pure metal by van Arkel, de Boer and Fast in 1925, is mute evidence of the difficulty encountered in the production of the pure metal. These years were not without effort, however. In 1824 Brezelius[1] attempted to reduce potassium fluozirconate with sodium; the resulting powder probably was an oxide. Troost[2] repeated this work in 1865, and also attempted to reduce the chloride with sodium and magnesium, investigated the reduction of sodium zirconium fluoride with aluminum, and studied electrolysis of the double fluorides. He was unable to produce any material that was malleable or ductile or that showed any corrosion resistance. It seems probable that his end products were mostly the lower oxides of zirconium. In 1910 Lely and Hamburger[3] reacted zirconium tetrachloride with sodium in a bomb and succeeded in producing a few malleable pellets. Marden and Rich[4] in 1925, made brittle metal about 99.5 per cent pure by reducing the double fluoride with aluminum.

Although early workers experimented with the reduction of boron silicon, and tungsten chlorides

Table I. World Production of Zirconium Ores and Concentrates, by Countries, 1946—53, in Short Tons

Country	*1946*	*1947*	*1948*	*1949*	*1950*	*1951*	*1952*	*1953*
Australia*	13891	24165	25017	23486	24120	47006	32893	33200†
Brazil (exports)†	4909	4385	4011	2977	3325	3854	2425	1206
Egypt	4	—	104	141	105	4	133	§
Fr. West Africa	-	43	211	270	242	29	—	992
India	522	¶	¶	¶	¶	¶	¶	¶
United States*	7946	¶	¶	¶	¶	¶	¶	¶

*Estimated zircon content of all zircon-bearing concentrates.
†Estimate.
‡Chiefly baddeleyite.
§Data not available.
¶Not available for publication.

on a hot wire in a hydrogen atmosphere it remained for van Arkel, de Boer and Fast, [5-7] to prepare the first truly pure zirconium in history and to determine its properties at the University of Leyden in 1925. Their original experiments were carried out in small evacuated glass vessels. Capacity of the reactors and heat dissipation problems resulting from high current demands limited their output to about 250 grams per vessel.

Von Zeppelin[8] in 1940 was the first to make ductile zirconium by magnesium reduction of zirconium tetrachloride. He heated a mixture of sodium chloride, zirconium chloride, and magnesium turnings in a cast-iron crucible suspended in a gas-fired furnace. No further progress was made using the magnesium-reduction process until 1945 when personnel of the Bureau of Mines, Albany, Oregon, began investigating the possibility of developing an economical method for producing the ductile metal. The exclusion of air during the critical steps of the process made the production of commercial quantities of ductile zirconium possible.

Commercial Production Methods

At present only three methods appear to be of commercial significance; in order of importance they are: (1) the reduction of the halides with sodium, calcium, or magnesium; (2) the decomposition of the halides on hot filaments; and (3) fusion electrolysis of the double fluorides.

Reduction of Halides

Reduction of zirconium tetrachloride with sodium and calcium has met with varied success. To date, magnesium has proved most acceptable. Details of the magnesium reduction process as developed by the Bureau of Mines and employed by the Carborundum Metals Company, Akron, New York, will be discussed later in the presentation.

Iodide Process

In 1940 the Foote Mineral Company of Philadelphia, Pennsylvania, acquired the American rights to the patents of the Phillips Lamp Works, Eindhoven, Netherlands, to produce zirconium metal by the iodide-decomposition process. Although metal of extremely high purity is produced by this method, the process must be considered as a refining step rather than a primary reduction method, since the starting material must be a fairly pure metal. The original work was carried out in glass vessels. Subsequent adoption of metal reaction vessels permitted larger charges, better accessibility, easier handling, and improved temperature control. Filament design and shape were altered to permit longer filaments with a result that larger crystal bars were grown. Reaction temperatures were controlled by the regulation of filament current and external heating or cooling in a thermostatically controlled salt bath. One of the major problems encountered in going to large size was that of fastening filaments to electrodes. The cooling effect of large clamps on small filament wires caused cooling and slowing down of the deposition rate. High current demands caused the filaments to melt when they were smaller than the larger areas containing the deposits. This difficulty was overcome by several ingenious devices, such as tapered electrode holders, and in the later Westinghouse Electric Corporation development did not pose an insurmountable problem.

The over-all efficiency of the operation is said to be about 95 per cent although only 8 or 10 per cent of the zirconium charged is consumed by a single run. The balance remaining in the vessel is washed and screened to remove fines and then charged back into the reactor.

The purity of the final as-deposited rods depends on the removal of all contaminating gases from the system and the purity of the starting materials.

The most important property of the crystal bar zirconium and the one which is proclaimed most widely is the purity of the final product which is reported to be as follows:

Element	*ppm*	*Element*	*ppm*
Silicon	30	Magnesium	10
Iron	200	Lead	10
Aluminum	30	Nickel	30
Titanium	10	Chromium	30
Calcium	50	Nitrogen	10
Manganese	10	Oxygen	200
Copper	55		

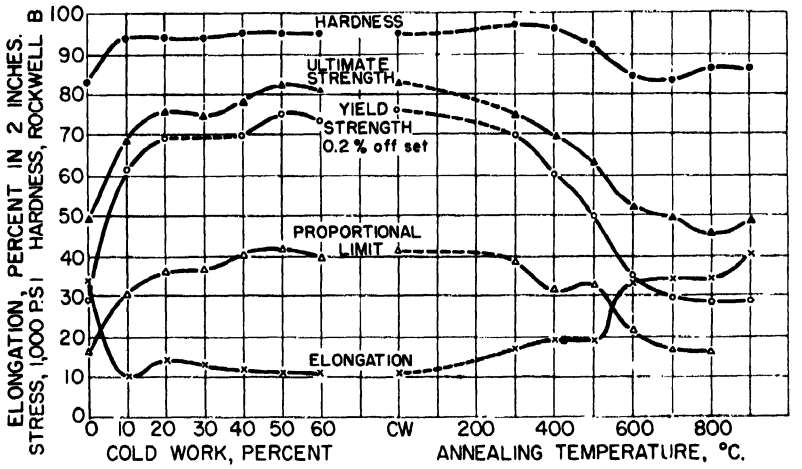

HARDNESS
ULTIMATE STRENGTH
YIELD STRENGTH 0.2 % off set
PROPORTIONAL LIMIT
ELONGATION
ELONGATION, PERCENT IN 2 INCHES. STRESS, 1,000 P.S.I. HARDNESS, ROCKWELL B
0 10 20 30 40 50 60 CW
COLD WORK, PERCENT
200 400 600 800
ANNEALING TEMPERATURE, °C.

Figure 1. Effect of cold work and annealing temperature on the tensile properties of arc-melted Kroll-process zirconium

This analysis is not final, however, since the bars require melting before they can be made into useful shapes. Melting invariably is a major source of contamination, and the ingots melted from crystal bar usually have analyses similar to ingots prepared from sponge.

The greatest deterrent to the process as it is used today is the necessity of using magnesium-reduced sponge as a feed, which prevents the two products from competing on a cost basis. Thus the only hope for crystal bar to compete with sponge hinges on the development of a cheap feed material. The most likely source is an impure metal produced by the reduction of the oxide by calcium. Although the metal thus produced is not ductile, it is said to be suitable for cell feed. The most attractive feature of this method is the direct reduction of the oxide, which is the form resulting from hafnium purification.

Electrolysis

Although the electrolysis of aqueous solutions has never been attractive, the electrolysis of zirconium compounds in fused salt baths has produced small quantities of the metal. Troost[2] and Marden and Rich[4] studied the process, and Driggs and Lillendahl[9] patented a process for the electrolysis of fluoride baths. Kroll [10] *et al.* and Steinberg, Sibert, and Wainer[11] have made additional investigations which resulted in the production of small quantities of good grade metal.

The investigators followed three main patterns in their studies: (1) fused baths of alkali chlorides and potassium fluozirconate; (2) fused baths of alkali chlorides containing zirconium chloride; (3) fused baths of alkaline earth chlorides containing potassium fluozirconate.

Horizons, Inc. reports that ductile zirconium was obtained by electrolysis of fluozirconate at operating temperatures of 800–850°C. The metal had a hardness of Rockwell (R_A) 47 to (R_A) 51, or Brinell 145–170. The oxygen content was given as 0.03 to 0.07 per cent; carbon content as 0.02 to 0.035 per cent; and nitrogen as about 0.0035 per cent or less.

The electrolysis of fused salts shows promise as a commercial method for producing zirconium. As yet it has not passed the pilot plant stage. One of the major deterrents to its success is the necessity for leaching the mixed salt-metal product, with the inevitable danger of oxygen contamination.

Other Methods

Although calcium has been shown to be one of the most favorable reducing agents for zirconium oxide, no commercial method for the production of significant amounts of pure metal has been developed.

Kelley[12] states that the effectiveness of lithium, sodium, magnesium and calcium in removing oxygen from zirconium depends directly upon the free energies of formation of their oxides. The effectiveness of the metals at various temperatures is shown in the following tabulation.

Free energies of formation (kcal)

T°K	Na_2O	Li_2O	MgO	CaO	ZrO_2
500	—83.0	—127.7	—130.9	—138.2	—119.2
800	—72.4	—117.3	—123.1	—130.9	—112.5
1000	—65.5	—110.2	—117.7	—126.0	—108.0
1200	—58.2	—102.9	—112.1	—121.1	—103.6
1400	—45.1	— 95.7	—106.4	—115.8	— 99.1
1600	—32.2	— 92.0	— 96.3	—110.7	— 94.8
1800	—19.6		— 86.3	—104.8	— 90.5
2000	— 7.2		— 76.4	— 95.6	— 86.2

The reaction $ZrO_2 + 2\,Ca = ZR + 2\,CaO$ $\Delta H_{298} = -45{,}000$ cal is highly exothermic and the rate of reaction is controlled by the addition of $CaCl_2$ to the charge. Kalish[13] states that this method is used to produce fine powder for powder metallurgy, radiotube getters, and flash powder. The charge contains from 20 to 100 per cent excess calcium. Specially prepared, high-purity calcium chloride is added as a moderator to control the violence of the reaction and to protect the walls of the reaction vessel. The reduction is initiated by heating the charge to about 1000°C.

Although usually classified as a bomb reaction, the process may be carried out in an open vessel.

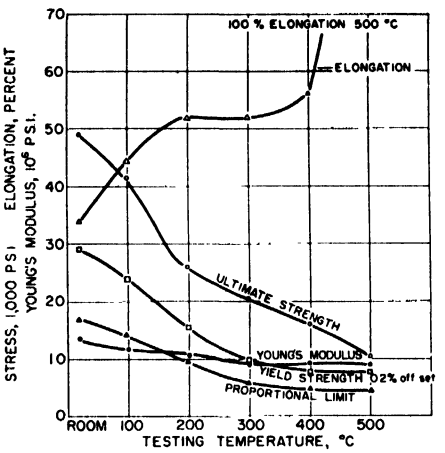


Figure 2. Effect of temperature on the tensile properties of arc-melted Kroll-process zirconium

Protection from atmospheric contamination is mandatory. The reaction mass is crushed, leached with dilute acid, rinsed with water, and dried carefully. The presence of substantial amounts of oxygen in the leached powder is attributed to oxygen pickup during the leaching and drying cycle. The oxygen content varies from 0.3 to 1.0 per cent. Nitrogen contamination is another serious drawback to this method. The nitrogen is introduced by the calcium, and the necessity for high-purity calcium is one of the major disadvantages of the process.

Lilliendahl, *et al.*,[14] in a search for an analytical method for determining oxygen in zirconium, showed that oxygen could be removed by heating the metal in a bath of molten calcium. Preliminary work at the Bureau of Mines, has demonstrated that substantial amounts of oxygen can be removed from machine chips and turnings by exposing them to calcium vapor. The resulting CaO is removed by leaching in dilute HCl. It is believed that a process can be developed for the reclamation of industrial scrap that will be of material value in cutting down scrap loss.

To date, the production capacity of all the methods discussed has been limited by the necessity of batch operation. Until some innovation is realized whereby a continuous production can be accomplished, the metal will remain as an expensive material. Two methods have been suggested for continuous operation. In 1949 the National Research Corporation conducted extensive research on the decomposition of ZrI_4 in an electric arc with the reduced metal being collected in a molten pool of zirconium. The ingot was withdrawn as it grew. Conversion rates generally were low. Appreciable contamination was encountered due to corrosion of the reaction vessel and the problem of iodine and excess iodide recovery were difficult to solve. The process never reached a commercial stage.

Attempts to deposit metal from a stream of zirconium tetra-iodide on an inductively heated revolving disc were made by the Massachusetts Institute of Technology metallurgical project. Low efficiencies and operating difficulties prevented the construction of pilot plant size equipment.

PROPERTIES OF ZIRCONIUM

Zirconium with its transparency to low speed neutrons coupled with its high resistance to corrosion at medium temperatures has found its greatest use in the construction of nuclear reactors. This field of use has dominated the output of high-purity zirconium almost completely, resulting in very little metal being used for other purposes. The emphasis placed on zirconium for use in nuclear-powered engines has precipitated, in a relatively short period of time, an abundant amount of research and investigation. Many of the more common properties and physical constants are available, some of which are listed below:

Atomic number: 40[15]
Atomic weight: 91.22[15]
Atomic radius: zero charge 1.60, 1.62Å; +4 charge 0.80, 0.89Å[15]
Density: 6.499 grams per cc at 26.4°C[16]
Crystal structure: alpha-hexagonal close packed and beta-body centered cubic[17]
Alpha to beta transformation temperature: 865°C[17-19]
Melting point: 1860°C[20,21]
1845°C[19]
Boiling point: over 2900°C[22]
Coefficient of thermal expansion: 4.9×10^{-6}/°C[19]
Thermal conductivity: 0.040 cal/°C/cm/sec[23]
Thermal capacity: C_p 0.069 cal/gm/°C (25 to 100°C)[19]
Entropy: 0.18 ± 0.08 cal/mole°K A + 25°C[24]
Enthalpy: 5.0 cal/gm at 100°C, 12.0 cal/gm at 200°C, 19.2 cal/gm at 300°C, 26.9 cal/gm at 400°C, 35.0 cal/gm at 500°C, 43.5 cal/gm at 600°C[24]
Vapor pressure: 0.01 mm. Hg at 2000°C, and 900 mm Hg at 3600°C[25]
Resistivity: 39.7 microhm cm (20°C)[19]
Temperature coefficient of resistivity: 0.0044/°C (20°C)[26,27]
Pressure coefficient of resistivity:
$\Delta\rho/\rho = 0.431 \times 10^{-6}p + 6.7 \times 10^{-12}p^2$ at 30°C
$\Delta\rho/\rho = 0.601 \times 10^{-6}p + 5.8 \times 10^{-12}p^2$ at 75°C[27]
Electrochemical equivalent for valence of 4: 0.2363 mg/coulomb[28]
Hardness: Brinell 125–145 arc cast Kroll process (unpublished data, Bureau of Mines, Albany, Oregon)
Tensile strength: 50,000 psi, annealed sheet Kroll process[29]
Yield strength: 0.2% offset 30,000 psi, annealed sheet Kroll process[29]
Proportional limit: 17,000 psi, annealed sheet Kroll process[29]
Young's modulus: 13.5×10^6 psi, annealed sheet Kroll process[29]
Elongation in 2 in.: 34 per cent, annealed sheet Kroll process[29]

Tensile and Impact Properties

Tensile Properties of Cold Rolled and Annealed Sheet

Cold working of zirconium results in increasing the ultimate strength, yield strength, and proportional limit values along with the hardness. Figure 1 shows the variation in hardness, ultimate strength, yield strength, proportional limit, and elongation of Kroll process zirconium with increase in cold work and annealing temperatures. Over 90 per cent of the increase in hardness and strength, due to work hardening, occurs between 0 and 10 per cent cold

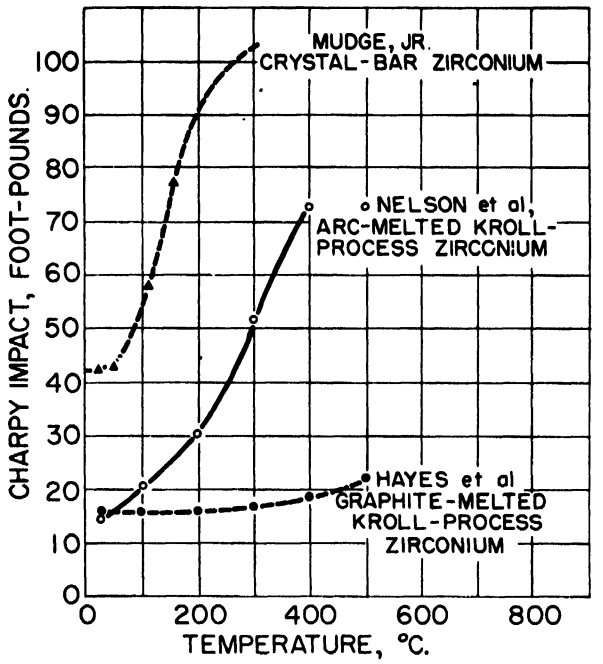


Figure 3. Effect of temperature on the impact-strength of zirconium

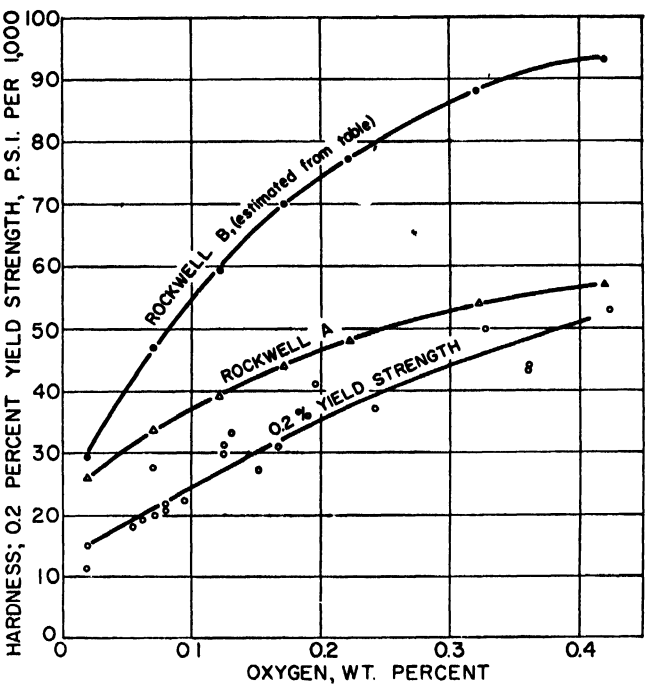

ROCKWELL B, (estimated from table)
ROCKWELL A
0.2% YIELD STRENGTH
HARDNESS; 0.2 PERCENT YIELD STRENGTH, P.S.I. PER 1,000
OXYGEN, WT. PERCENT

Figure 4. Effect of oxygen on hardness and yield strength of zirconium

work, as shown by the hardness, strength, and elongation curves. Young's modulus is not affected appreciably by cold working.

Annealing of zirconium at increasing temperatures results in a gradual decrease in ultimate and yield strengths. Elongation values change gradually up to 500°C.

Tensile Properties at Elevated Temperatures

The ultimate strength of zirconium, as shown in Fig. 2, decreases from 49,000 psi at room temperature to [1]1300 psi at 500°C, and the yield strength at 0.2 per cent offset decreases at nearly a constant rate from 29,200 psi at room temperature to 7800 psi at 400°C. The proportional limit shows a curve similar to the yield strngth, decreasing from 16,500 psi at room temperature to 4900 psi at 400°C and 4400 psi at 500°C. The elongation values increased from 34 per cent at room temperature to 100 per cent elongation at 500°C.

"V" Notch Charpy Impact Values

Figure 3 shows the effect of temperature on the notched bar impact value of three different types of zirconium.

The impact values shown for arc-melted Kroll-process zirconium are a distinct improvement over the values of graphite-melted material of Hayes, Dilling, and Roberson.[80] This undoubtedly is due to the increased purity of the arc-melted material and probably is dependent partially on its lower carbon content. Arc-melted Kroll-process zirconium has impact values considerably lower than crystal-bar zirconium reported by Mudge,[81] and could be accounted for by a difference in hydrogen content.

Hardness

The hardness of crystal bar metal as deposited runs 25–30 R_B (65–70 Brinell 500 kg), while the Kroll-process zirconium, as presently produced, has a hardness of R_B 77–80 (Brinell 140–150, 3000 kg).

The curves of hardness vs oxygen content are shown in Fig. 4. The hardness is seen to increase rapidly at the low percentages and to continue to increase, but at a slower rate, as the oxygen additons increase.

Nitrogen has the same general effect as oxygen. The hardness increases rapidly with the increase in

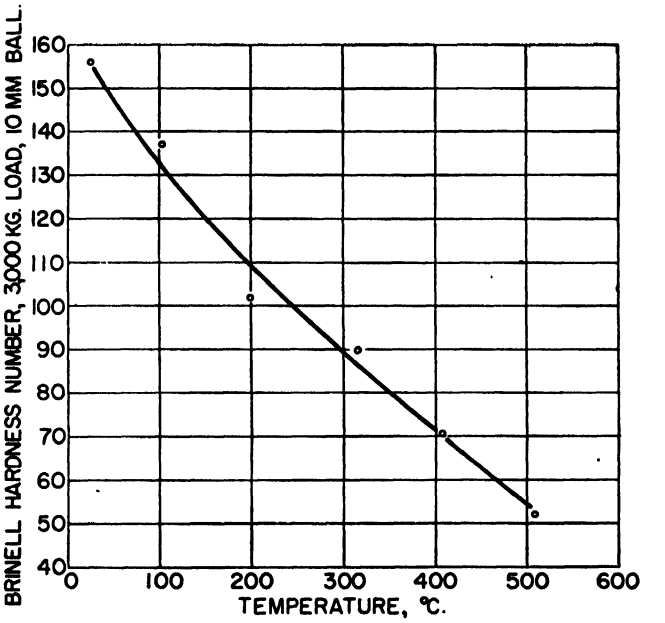


Figure 5. Hot hardness of arc-melted Kroll-process zirconium

nitrogen content. A given amount of nitrogen is more effective in increasing the hardness than an equal amount of oxygen, but in general the use of this element to increase the hardness is not to be recommended, since the resistance to oxidation and corrosion is impaired rapidly.

The effect of annealing temperature and cold work on the hardness of Kroll-process zirconium is shown in Fig. 1.

Zirconium hardens rapidly when cold worked, especially during the first 10 per cent of cold work where 90 per cent of the work hardening is effected. Examination of the curves of Fig. 5 shows that zirconium has an abnormal drop in hardness at relatively low temperatures. The Brinell number is halved upon heating zirconium to 300°C.

Creep

Brunstetter and Alexander[32] evaluated the creep characteristics of vacuum annealed crystal bar zirconium at room temperature (25°C) and at 200°C. A stress of 50,000 psi will produce a minimum creep rate of 1 per cent in 1000 hours at room temperature. This compares favorably with that of low carbon steel at room temperature. At 200°C, however, the creep strength drops to half of the room temperature value while the creep strength of low carbon steel remains practically the same. The rapid loss of creep strength indicates that the pure zirconium metal will not be a useful structural material for high temperatures even though it has a high melting point.

Elastic Properties and their Anisotropy

Compressibility

Zirconium is one of the more incompressible substances. In two determinations of volume decrement at 10,000 kg/cm^2, Bridgman[33] obtained values of 0.0103 and 0.0111.

Young's Modulus

Young's modulus has been reported to be $11.3 \pm 2.3 \times 10^6$ psi for annealed or as-deposited iodide material by Boulger.[34] Reynolds,[35] using the ultrasonic pulse technique, has measured Young's modulus on both Bureau-of-Mines and crystal-bar material. The values obtained by him for annealed material are 13.9×10^6 psi for Bureau-of-Mines zirconium, and 12.8×10^6 psi for crystal-bar.

Poisson's Ratio

The determinations of Poisson's ratio for both Bureau-of-Mines zirconium, and crystal-bar zirconium have been carried out by Reynolds.[35] He reports values of 0.33 and 0.35.

Shear Modulus

For values of the modulus of shear, Reynolds,[35] reported values 5.24×10^6 psi for Bureau-of-Mines material and 4.76×10^6 psi for crystal-bar zirconium.

Crystal Structure and Crystallography of Transformation

Crystal Structure—Alpha and Beta

The structure of zirconium as being a hexagonal system was established by Hull[36] in 1921. Zwikker,[37] using electrical resistivity measurements, found evidence of a high-temperature phase. This was identified as a body-centered cubic structure with a_0 equal to 3.61 kX units at 867°C by Burgers.[38] Precision determinations of the lattice parameters of the low temperature phase have been made on high-purity crystal-bar zirconium by Treco.[39] He reports the following data:

a_0 3.2256 ± 0.00014 kX units
c_0 5.1370 ± 0.00036 kX units
c/a 1.5926

Miscellaneous Properties

Magnetic Susceptibility

Zirconium is paramagnetic in both its allotropic forms.

Emissivity

The coefficients of spectral emission as reported by de Boer[20] are:

ϵ red (0.652) = 0.48 under 1500°K
ϵ red (0.652) = 0.43 above 1500°K
ϵ green (0.541) = 0.50 under 1500°K
ϵ green (0.541) = 0.46 above 1500°K

Photoelectric Properties

The photoelectric threshold of pure zirconium as measured by Rentschler and Henry[48] is about 3150 Å. From this wavelength the photoelectric work function is found to be 3.9 ev. They also showed that the work function could be lowered by contamination with oxygen, nitrogen and hydrogen.

Corrosion Resistance of Zirconium

One of the outstanding properties of zirconium is its excellent corrosion resistance to many chemical corrosives. Among the more-or-less special metals, the corrosion resistance to acids and other aqueous metals is roughly in the order: tantalum, zirconium, niobium, titanium, tungsten, and molybdenum.

Corrosion of Zirconium in Liquids

Table II shows a comparison of the corrosion properties of zirconium, titanium, and tantalum. This table was compiled by Wick[41] from studies made by Golden of the Bureau of Mines at College Park, Maryland, and others.

Golden[42] has shown that zirconium was fully resistant to attack at temperatures up to 100°C by the following solutions:

Solution	*Per cent*
Stannic chloride	24
Manganous chloride	20
Nickel chloride	20
Sodium chloride	Saturated solution
Ammonium chloride	Saturated solution
Calcium chloride	25
Barium chloride	20
Zinc chloride	20
Aluminum chloride	25

Substitute Ocean Water

Golden's[42] work also has indicated that tests at 35°C showed zirconium to be completely resistant in substitute ocean water. Other tests, which also exposed zirconium to 30-day ocean-water tests, showed no corrosion. Other sea-water tests at Kure Beach, North Carolina, have shown no corrosion effects after several years' exposure.

Tests performed on actual sea water at the US Naval Experiment Station, Annapolis, Maryland, confirmed these results closely.

Organic Acids

Golden's[42] corrosion tests up to 100°C in the following organic acids at the concentrations indicated showed that zirconium was resistant almost completely to attack in all these acids except di- and trichloroacetic acids at boiling temperatures. Oxalic acid showed slight attack on zirconium. Zirconium was corrosion resistant to the following acids at room temperature:

Organic acids	*Per cent*	*Organic acids*	*Per cent*
Formic acid	10–90%	Lactic acid	10–85
Acetic	5–99.5	Tannic acid	25
Monochloroacetic	100	Oxalic acid	0.5–25
Dichloroacetic	100	Tartaric acid	10–50
Trichloroacetic	100	Citric acid	10–50

Organic Compounds

Golden's[42] work also includes corrosion results of zirconium in several organic compounds as follows:

		Corrosion resistance		*Catalytic effect on decomposition*
Compound	*Temperatures*	*Liquid zone*	*Vapor zone*	
Chloroform	Boiling	Complete	Complete	None
Ethylenedichloride	Boiling	Complete	Complete	None
Trichloroethylene	Boiling	Complete	Complete	None
Tetrachloroethylene	Boiling	Complete	Complete	None
Tetrachloroethane	Boiling	Complete	Complete	None
Aniline hydrochloride	Boiling	Complete	Complete	None

Anhydrous hydrazine: Zirconium was found to be completely resistant to 95 per cent solutions of anhydrous hydrazine[43] at room temperatures.

USE OF ZIRCONIUM

Zirconium shows promise of becoming one of the most versatile of metals. This versatility stems from its physical, chemical, and nuclear properties, the combination of which are not matched by any other metal. It is of interest particularly in the nucleonic field where its prominence has been displayed quite forcibly.

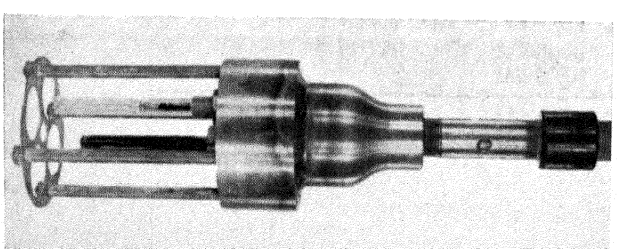


Figure 6. Zirconium pH electrode assembly fabricated to replace one shown in Fig. 7 support rods were in use 10 months

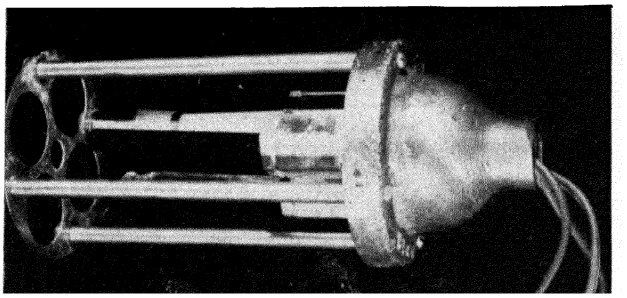


Figure 7. Type 316 stainless steel pH electrode assembly after 10 months' service in zirconium phthalate slurry; rods supporting bottom guard are new

Nuclear Reactors

Little has been reported about the atomic or nuclear uses of ductile zirconium because of the curtain of secrecy that surrounds all work of this type. However, recent information in the literature cites the reasons for the nuclear interest in zirconium.

Miller[44] states, "The properties of zirconium make it particularly useful in thermal reactors, especially if they are to be used for power production, where neutron economy and regeneration of fuel are important." He states further, "In addition to a low neutron-absorption cross section, other stringent demands are placed on structural materials and components in power reactor systems. These include: (1) mechanical strength and stability under the severe stresses resulting from high thermal gradients; (2) leak-tight reliability in high-temperature, high pressure, corrosive, dynamic, and radioactive cooling systems; (3) resistance to mechanical damage by radiation; (4) limited formation of high-activity products by nuclear reactions; and (5) adaptability to simple remote maintenance and repair."

Zinn[45] mentions beryllium, graphite, and zirconium as possible materials of construction for nuclear power stations and notes importance of full utilization of fuel through use of low-cross-section materials. Zirconium's transparency to neutrons is responsible for the important role the metal is playing in Westinghouse Electric Corporation's submarine nuclear reactor and in other water-cooled reactors of this type.

Saller[46] states, "At the present time, zirconium with its low thermal cross section, excellent corrosion resistance, good mechanical properties, and good fabricating qualities is the leading cladding and structural material for thermal reactors."

Chemical Equipment

Throughout the various processing steps necessary to the production of zirconium, there are many corrosive atmospheres, solutions, and conditions that defy the usual or normal materials of construction and make the Kroll process a useful proving ground for practical applications of zirconium.

Table II. Comparison of Corrosion Properties of Zirconium, Titanium and Tantalum*

	Zirconium	*Titanium*	*Tantalum*
Acetic acid	5%, 99.5%[7] 140°, 212°F[6] Excellent	5%, 10%[14] 68°F Excellent	All %[3] 68–735°F Excellent
Aluminum chloride	20%, 30% Room–boiling temp. Excellent	10%[10] 95%, 212°F Excellent	
Ammonium hydroxide	28%[2] Room–212°F Excellent	28%[19] Room temp. Excellent	
Aqua regia	65–140°F[1] Poor	65–140°F[1] Excellent	65–140°F[1] Excellent
Calcium chloride	20%, 30%, 50%[20] 68°, 120°, 212°F Excellent	10%, 25%[9] 95°, 212°F Excellent	
Chlorine-saturated H_2O	Room temp.[9] Excellent	Room temp.[9] Excellent	
H_2O-saturated chlorine	Room temp.[9] Poor	Room temp.[9] Excellent	
Citric acid	10%[2] Room–212°F Excellent		
Cupric chloride	1–25%[7] 95°F Poor	1–15%[8] 95°F Excellent	
Chromic acid	10%, 20%, 30%[20] 68°, 120°, 212°F Excellent	10%[14] Boiling Good	
Phosphoric acid	10-85%[6,2,1] Room—212°F[3] Excellent to fair	1–85%[8,1,11] 65–212°F Excellent in dil. at room–otherwise poor	85%[2,1] 290–410°F Excellent
Sodium chloride	3%[6,4] 95°F Excellent	3%[6] 95°F Excellent	
Sodium hydroxide	10%, 50%[20] Room–212°F[2] Excellent	10%, 40%[11,14] 175°F–boiling Good	5%, 40%[2] 212°, 230°F 40%—Poor
Sulfuric acid	10–96%[2,6,1] 65–212°F[3] Excellent in dilute Poor in hot conc.	5–65%[19,1,8] 65–95°F[10,6] Dilute-good[11] Conc.—Poor	20%–conc.[1,2] 65–570°F Excellent
Tartaric acid	10%, 25%, 50%[20] 68°, 120°F–boiling Excellent	50%[9] 95°F Excellent	
Methyl alcohol	99%[12] Boiling Excellent		
Ethyl alcohol	95%[6] Boiling Excellent	95%[6] Boiling Excellent	
Carbon tetrachloride	100%[20] Room temp–120°F Excellent	1–99%[14] Boiling Excellent	

(Continued on next page)

Table II. (Continued)

	Zirconium	*Titanium*	*Tantalum*
Tannic acid	10%[20] Room temp–boiling Excellent	25%[9] 95°F Excellent	
Ferric chloride	2.5–30%[4] 65–212°F[7] Poor[5]	1–20%[8] 65–212°F[10] Excellent[1]	5–30%[18] 65°F–boiling[1] Excellent
Formic acid	90%[7,20] 68°, 120°F–boiling Excellent	25–90%[19,9] 95°F–boiling Excellent	90%[7] 212°F Excellent
Hydrochloric acid	Dilute–excellent at all temps.[1,2] Conc. at room–exc. Conc. at boiling–poor[3]	5%–conc.[1,3,8] 95–212°F[10,18] Poor	19%–conc.[1,2] 65–212°F Excellent
Lactic acid	5–85%[4] Boiling Excellent	85%[9] 95°F–boiling Excellent	
Mercuric chloride	1% saturated[5] 95–212°F[7] Excellent[2]	1% saturated 95–212°F[10] Excellent	Saturated at 212°F[7] Excellent
Nitric acid	10% conc.[2,1] 65–212°F[3,12] Excellent[6]	5% conc.[1,3] 95–212°F[10,7] Good[11,16]	Conc.[1,2] 65–185°F Excellent
Oxalic acid	1–25%[5,7,2] 212°F[4] Excellent	1–25%[9] 95°, 212°F Poor	Saturated[2] Room–205°F Excellent
Phenol (carbolic acid)	25%, 50%, 100%[20] 68°, 120°F–boiling Excellent		Saturated[2] Room temp. Excellent
Potassium hydroxide	10%, 20%, 30% 40%[2]; Room–212°F[20] Excellent		230°F[2] 5%—excellent 40%—poor
White fuming nitric acid	Room temp.–160°F Good[20]	Room temp.–160°F Excellent	
Red fuming nitric acid	Room temp.–160°F Poor[21]	Room temp.–160°F Excellent	
Monochloroacetic	100%[4] Boiling Excellent	100%–boiling[4] Excellent	
Hydrogen peroxide	10%†[20] 120°F Excellent	Room temp.-30%[12] C.P.–poor A.C.S.–excellent	
Ammonium sulfate	Saturated† 120°F Excellent		
Aluminum sulfate	10, 30%†[20] Boiling Excellent		

*The tabulated data include solution concentration in per cent, temperatures in degrees F, and resistance to attack graded as follows: Excellent—Less than 0.0005 in. penetration per year; Good—0.0005 to 0.005 in. penetration per year; Fair—0.005 to 0.010 in. penetration per year; and Poor—More than 0.010 in. penetration per year.

†Complete corrosion tests currently being conducted in TAM Laboratory along with corrosion tests on acetone and stearic acid.

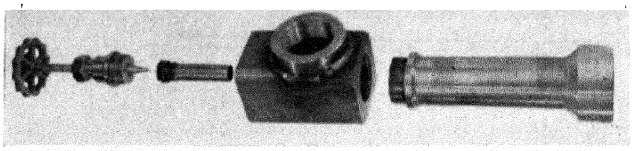


Figure 8. Exploded view of steam jet showing integral parts of ejector; all are made of zirconium, except handwheel

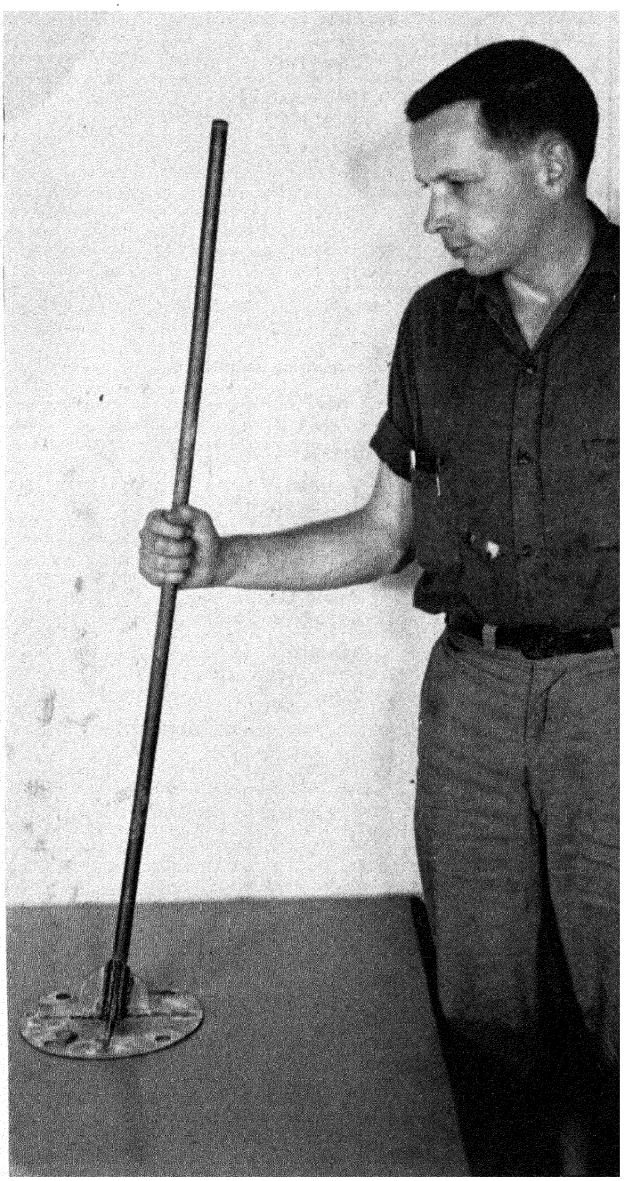


Figure 9. Zirconium thermowell used in feed-makeup tank

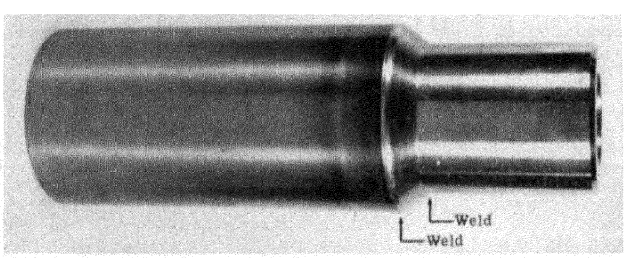


Figure 10. Zirconium hub for wood agitator

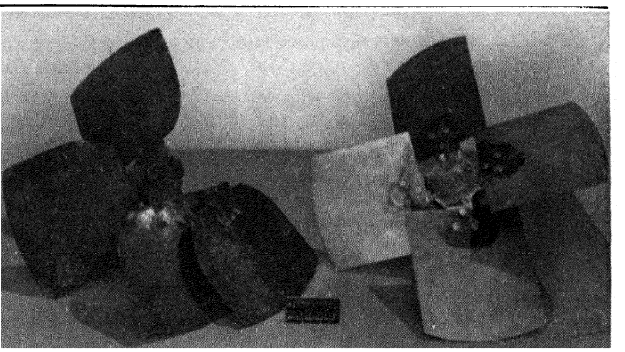


Figure 11. (left) plastic-coated steel exhaust fan that failed after 8 months exhausting hydrochloric acid fumes from feed filter press. (right) zirconium replacement fan, which now has 10 months' service without visible deterioration

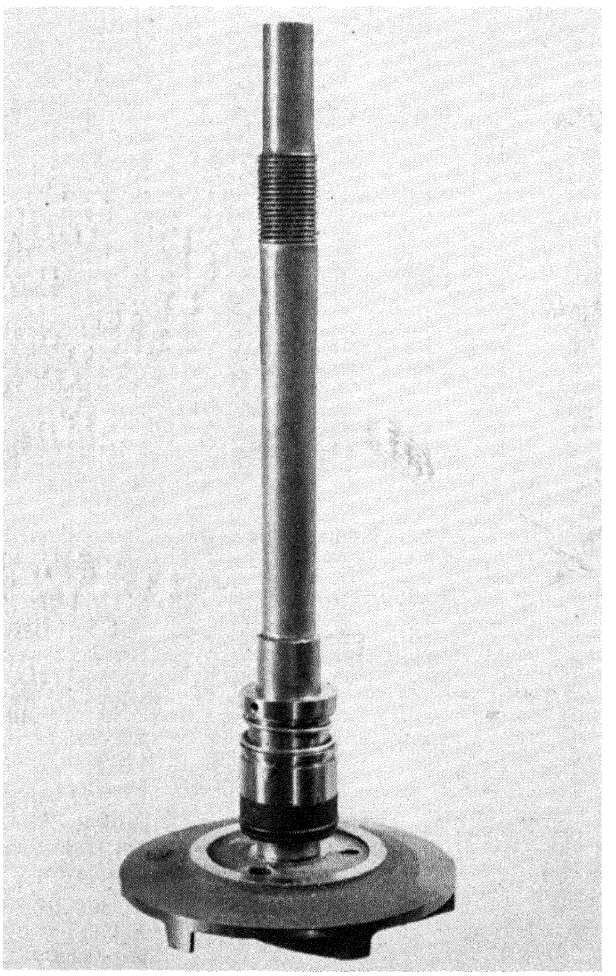


Figure 12. Zirconium mechanical seal shown on shaft of rotating element

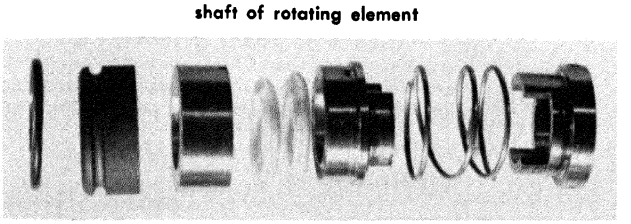


Figure 13. Exploded view of a zirconium mechanical seal. (From left to right: rubber "O" ring, graphite rub ring, zirconium rub plate, teflon seal, zirconium pressure plate, zirconium spring, and zirconium driving plate.)

In the past, ordinary steel construction was employed to expedite the fabrication of equipment needed to meet immediate production demands. In other instances, the finest material available was employed to meet definite conditions, with the knowledge that failure sometimes was inevitable over a period of time, in spite of careful selection.

Zirconium metal has been used with a high degree of success in solving these problems. This section describes those applications but does not attempt to evaluate the corrosion rates in the usual finite terms of a corrosion expert.

Zirconium-Lined Tank

A tank was designed to handle residues resulting from the purification and reduction of zirconium. It was believed that a glass-lined tank would be unsuitable for this purpose because of the abrasive qualities of the slurries to be handled. After 3-months' use in zirconium phthalate solutions, no evidence of corrosion was noted.

pH-Electrode Assembly

The assembly shown in Fig. 6 was fabricated from ingot zirconium to replace a standard type 316 stainless steel unit (Fig. 7), which failed after 10-months' service. This device is suspended in a weir box leading to a rubber-covered rotary vacuum filter. In normal operation, about half of the electrodes are submerged in the zirconium phthalate solution described in the previous application.

Steam-Jet Exhauster

This exhauster was fabricated to replace a 10-stage blower which could not be kept in serviceable condition, requiring overhaul at 10-day intervals. The impellers of this blower were type 316 stainless steel and the housing was cast iron. Fumes entering the blower had been passed through a scrubbing tower and a second trap containing iron turnings to remove the hydrochloric acid.

The steam jet pictured in Fig. 8 was put into use on February 1, 1953, and is still giving trouble-free performance.

Zirconium Thermowell

Two thermowells were fabricated of tubing and sheet zirconium for use in the zirconium chloride feed-solution make-up tanks. These replaced glass-covered thermowells. The tube shown in Fig. 9 has had 20 months in this service. A second unit has about the same length of service, 7 months in zirconium phthalate solutions.

Agitator Hub

The zirconium hub shown in Fig. 10 was fabricated from two ingots and a disk. This hub now has had about 2 years' service.

Exhaust Fan

A zirconium fan was fabricated to replace a plastic-coated fan that failed after 8-months' use. This fan exhausts hydrochloric acid fumes from a feed filter press. The zirconium unit shown in Fig. 11 has had about 10-months' service without visible signs of corrosion.

Mechanical Seal

A mechanical seal was fabricated for use on centrifugal pumps. Several good seals are available but none of them is easily adapted to pumps made of high-silicon cast iron, since they require that the inside surface of the packing glands of the pumps be machined by grinding to attain a suitable fit or surface.

The first seal, shown in Figs. 12 and 13, was put into use on February 17, 1953, and now has had 2 years of satisfactory service. About 15 of these are now in use.

Globe Valve

A zirconium globe valve (Fig. 14) is used to regulate the flow of gas being evacuated from furnaces in the reduction unit. The fumes are essentially hydrochloric acid. Length of service is estimated at 2 years.

Zirconium Pipe Fittings

Zirconium pipe fittings and flanges are being used in many services throughout the process without failure.

Spray Nozzles

The use of zirconium spray nozzles in noxious gas scrubbers is an important application, as they can

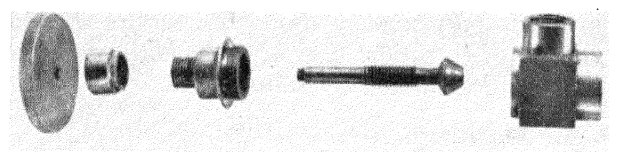


Figure 14. Exploded view of globe valve

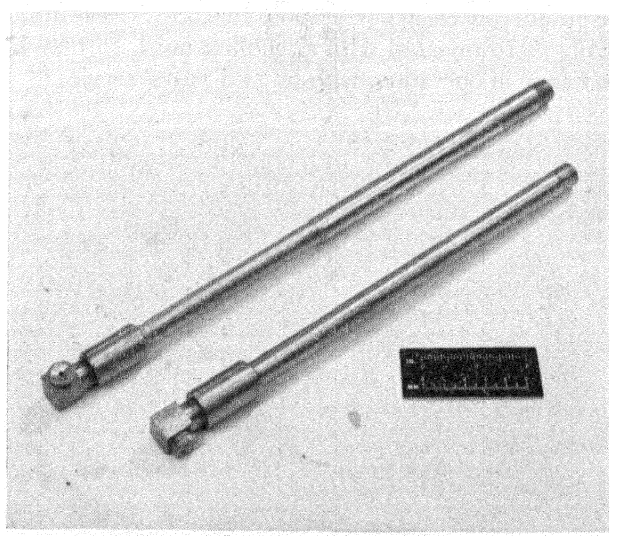


Figure 15. Zirconium spray nozzles, couplings, and pipe after 14 months' service in exit-chlorine scrubbing tower. (In contact with wet chlorine and chlorides of hydrogen, iron, aluminum, silicon, and titanium. Top pipe is pure nickel after 6 weeks' service.)

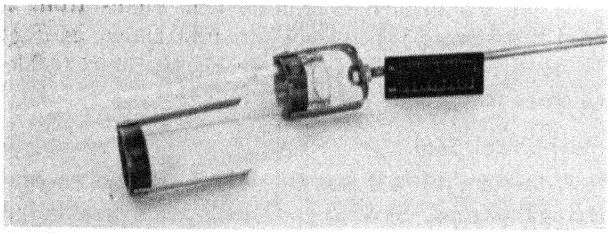


Figure 16. Zirconium clamp on 1-inch glass pipe and rod used to raise and lower column interface control mechanisms

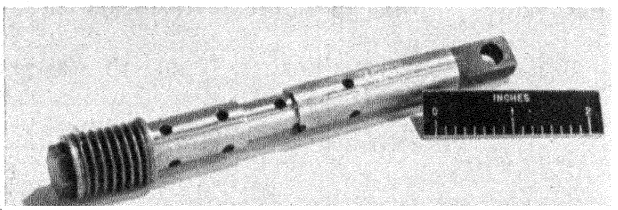


Figure 17. Zirconium hydraulic valve for use on forklift trucks

be fabricated easily from bar stock and are resistant to most corrosive gases encountered.

The first nozzles installed in 1949 are still serviceable after use in wet chlorine and hydrochloric acid fumes. The comparative resistance of nickel and zirconium is shown in Fig. 15.

Interface Control Mechanism

In June 1952, an interface control device was proposed that did not depend upon rubber or other flexible tubing. The use of zirconium in this application is illustrated in Fig. 16. The zirconium rods have had approximately 26-months' service without evidence of corrosion. Corrosives handled are 3.5*N* hydrochloric acid and 5*N* sulfuric acid.

Water Aspirator

In 1950 when the large-scale zirconium reduction unit was placed in operation, there was one brass aspirator on each purification furnace. These gradually were replaced with zirconium units, so that 12 are now in operation, with up to 3-years' service.

Hydraulic Valve Part

A zirconium hydraulic valve (Fig. 17) was put into use in hydraulic systems on forklift trucks. Standard mild steel valves furnished on the original equipment were found inoperative after 2-weeks' use, while the zirconium valve spools are still in service after 3 years.

Float Check Valve

This valve was fabricated to maintain a constant level in a solution head tank. It was in use 18 months, for zinc sulfate solutions ⅓ molar in sulfuric acid.

Rotary Filter Valve

A zirconium face plate, shown in Fig. 18, supports a hard-rubber valve on a 3 by 6 rotary filter, which is handling hot zirconium phthalate solutions. The temperature of about 70°C tends to warp the valve, so that leakage occurs between the rub plate and the rotary valve. This warpage is avoided by use of the zirconium backing or face plate.

Proportioning Pump Parts

Zirconium has been used successfully in repairing positive-displacement proportioning pumps. Ceramic plungers have been replaced with zirconium in several locations where hydrochloric acid, varying from 1 to 4*N*, is being pumped.

Laboratory Applications

Zirconium crucibles are being used at the Northwest Electrodevelopment Laboratory, Bureau of Mines, Albany, Oregon, for caustic fusions, where zirconium contamination is not objectionable and an iron determination is being made. Iron crucibles have an expectancy of 1 to 5 fusions. The zirconium crucibles are expected to last for a minimum of 25 fusions.

The utility of zirconium in analytical laboratories is outstanding. Probably the most important use is for caustic fusions where platinum and other wares corrode and fail. The crucibles pictured in Fig. 19 show only slight corrosion after 8 caustic fusions.

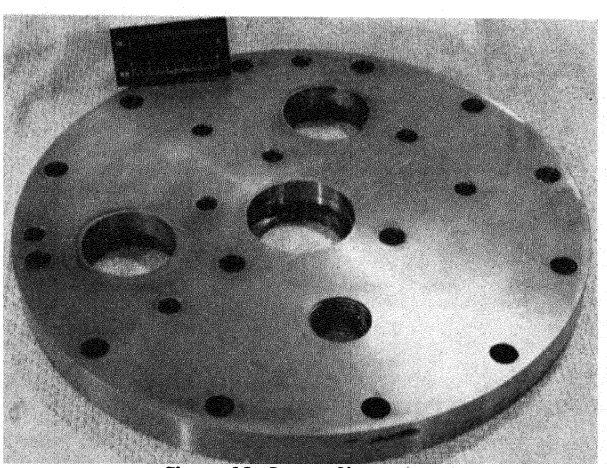


Figure 18. Rotary filter valve plate

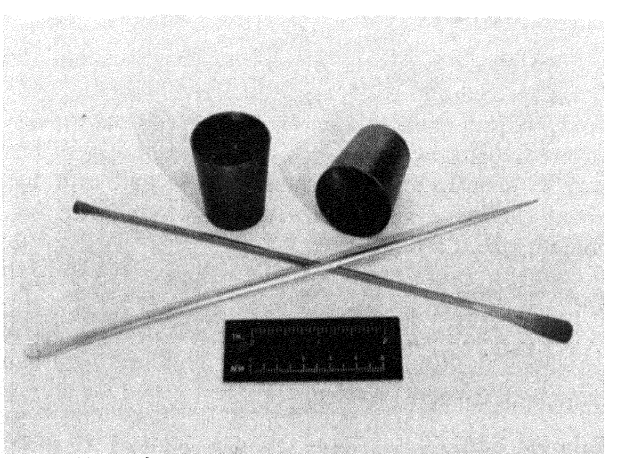


Figure 19. Zirconium crucibles after eight caustic fusions; zirconium spatulas

Table III. Zirconium Alloy Systems of the Fe-Fe_3C Type

System	Maximum solubility		Temperatures		Composition		First intermediate phase
	In alpha	In beta	Eutectoid °C	Eutectic °C	Eutectoid	Eutectic	
Zr-Fe	—	5.5	800	934	2.5	16	$ZrFe_2$
Zr-Ni	—	1.9	808	961	1.3	17	Zr_2Ni
Zr-Mn	—	6.5	795	1150	3.0	22.5	Zr_2Mn_2
Zr-Cr	0.1	6 to 8	805	1380	1.7	18	$ZrCr_2$
Zr-Mo	0.18	22	780	1520	7.5	31	ZrMo
Zr-W	—	8	850	1650	0.5	18	ZrW_2
Zr-Cu	0.2	3.8	822	995	1.6	21	Zr_2Cu

Alloys

The alloys of zirconium have been studied extensively the past few years and it is now known that zirconium has only a limited solubility for most metallic elements.

Zirconium, produced by the Kroll process at the Bureau of Mines, contains about 0.12 per cent oxygen and 0.005 per cent nitrogen. Until 1950, iodide-type zirconium, processed by the Philips Company at Eindhoven, Netherlands and the Foote Mineral Company, Philadelphia, Pennsylvania, contained 0.02 to 0.06 per cent oxygen. The use of Kroll-process sponge as feed material for the iodide refining process reduced the oxygen content to less than 0.01 per cent for Grade I material. Grades II and III contain more impurities, and the oxygen content of Grade III is between 0.03 and 0.10 per cent. Zirconium prepared by calcium or sodium reduction, generally is of inferior quality compared to that made by the Kroll or iodide process.

Most of the alloy research work has been done using either Kroll- or iodide-process zirconium. Bureau of Mines workers used Kroll process material in determining the Zr-Fe, Zr-Cr, Zr-Ni, Zr-Mn, and Zr-Ti systems. Armour Research Foundation investigators used Grade III crystal bar for most of their work involving the Zr-Sn, Zr-Al, Zr-Cr, Zr-W, Zr-Mo, Zr-Cu, and other systems. Critical points were checked with Grade I crystal bar and found to be in substantial agreement. Zirconium used prior to 1951 contained 1 to 2 per cent hafnium. Because of the similarity of the metals, it is believed that this has little effect on the critical points of the systems investigated.

Melting of zirconium-rich alloys represents another possible source of oxygen contamination, both by pickup from the crucible and absorption from the atmosphere. Older work using alumina crucibles is of questionable value because of oxygen contamination. Most of the modern zirconium alloy work involved use 50 to 100 gram melts prepared by tungsten-tip arc melting in a von Bolton type furnace.

Methods

Over 90 per cent of the investigations on zirconium phase diagrams have occurred during the past five years and have therefore benefited by the application and use of modern techniques and equipment. One of the principal deterrents to the attainment of accurate data has been contamination of zirconium by oxygen. Because of the avidity with which oxygen combines with zirconium, all thermal operations require the use of either a vacuum or an inert atmosphere.

The principal methods used in determining the phase systems were metallography, thermal analysis (including dilatometry), melting point determination, and X-ray diffraction.

A few elements show extensive solubility in the alpha form of zirconium and the principal ones of this class are shown in Table IV.

Systems

Table III is a summary of the salient features of a number of zirconium alloy systems of the Fe–Fe_3C type.

Table IV. Zirconium Alloy Systems Showing Extensive Alpha Solubility

System	Max. solubility, wt %		1st peritectic °C	1st peritectoid °C	1st intermediate phase
	In alpha	In beta			
Zr-Al	3.5	9.5	1350	940	Zr_2Al
Zr-Sn	9	21	Eut.	980	Zr_4Sn
Zr-O	29	10.5	1940	—	ZrO_2
Zr-N	25	5.0	1880	—	ZrN

REACTOR-GRADE ZIRCONIUM

Zirconium production on a tonnage basis was developed in the United States to meet the requirements of the atomic reactor program.

During development, it was established that zirconium chloride, free from hafnium, reduced to zirconium sponge by the Kroll process and melted to ingot by the consumable-arc process, using a water-cooled copper crucible, would meet the physical and chemical requirements for use primarily as a sheathing material in atomic reactors.

Production of zirconium on a large scale by the Northwest Electrodevelopment Laboratory, Bureau of Mines, Albany, Oregon is an anomaly which justifies some explanation.

The reduction of titanium tetrachloride with magnesium in an inert atmosphere, as perfected by Mr. W. J. Kroll prior to 1940, aroused renewed interest in zirconium and, in 1945, developmental work on this metal was initiated under the technical direction of Kroll. Preliminary results were promising and in February, 1947, a pilot plant with a capacity of 60 pounds of zirconium metal sponge per week was put in operation. Shortly thereafter the Atomic Energy Commission requested production of one ton of zirconium metal sheet, with the provision that it have a low-hafnium content. The Bureau of Mines was furnished with a supply of Brazilian baddeleyite ore, containing less than one per cent hafnium with respect to zirconium, from which was made about 2700 pounds of relatively low-hafnium zirconium sheet of 0.080-inch thickness for test purposes. This was accomplished by melting zirconium sponge in a graphite crucible, hot rolling the ingot in an iron sheath, and finishing by cold rolling.

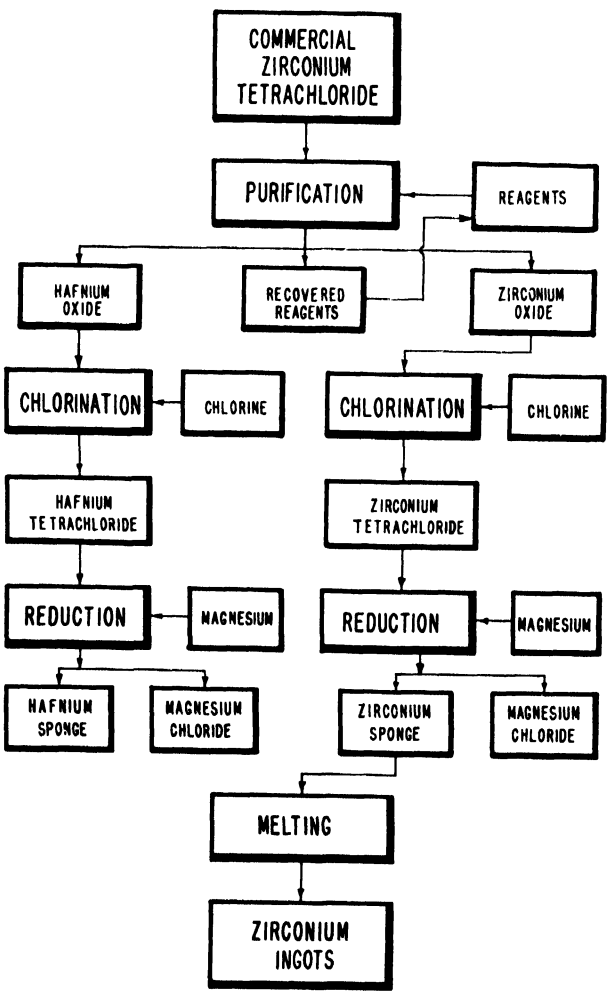


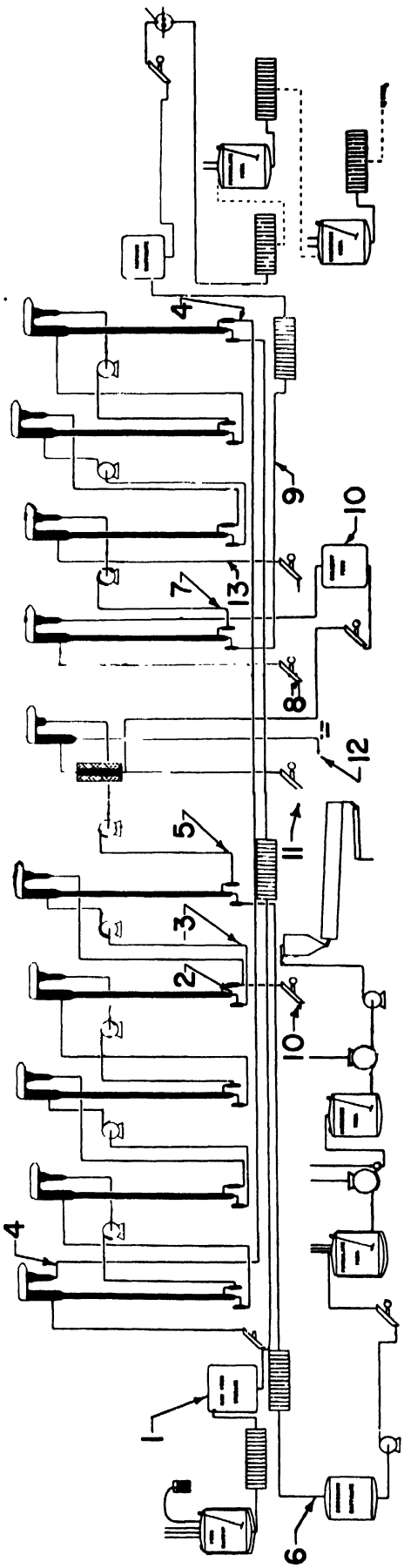
Figure 20. Zirconium-production flowsheet

Concomitantly, contractors for the Atomic Energy Commission developed a method for separating hafnium from zirconium and, in cooperation with the Atomic Energy Commission and Bureau of Ships of the Navy, a larger pilot plant was erected to produce zirconium from very low-hafnium zirconium tetrachloride furnished by the Commission. Production of zirconium sponge in the larger pilot plant of 500 pounds per week capacity started in June 1949.

Major attention was given to quality control. Hafnium was only one of the troublesome impurities. Appreciable quantities of nitrogen caused embrittlement and loss of corrosion resistance. Oxygen caused embrittlement, and aluminum, titanium, and other metal impurities were suspected as corrosion promoters.

It was discovered that alloying metals including tantalum and tin gave advantageous properties. Zirconium, which had been little more than a laboratory curiosity, was establishing itself as a promising material of construction for nuclear reactors, but many unknowns in reduction methods, melting, quality control, and physical and chemical properties still existed.

It was found that the relatively high-purity zirconium sponge produced by the Kroll process could be refined by the van Arkel iodide-dissociation method to obtain exceptionally high-purity metal. Zirconium previously refined as van Arkel crystal bar had been low in oxygen and nitrogen and consequently ductile, but metallic impurities impaired the corrosion resistance. Industrial contractors of AEC took steps to expand refining capacity and install new refining furnaces as insurance that high-purity metal would be available. In May, 1950, ground was broken at the Bureau for the erection of a large zirconium sponge production plant and the first furnaces were placed in operation in August of that year. The Bureau plant was enlarged in January and again in October of 1951 to its present capacity of some 300,000 pounds of zirconium per year. During the same period, additional facilities were installed to convert low-hafnium zirconium oxide to zirconium tetrachloride by direct chlorination of the oxide with chlorine gas. A plant also was erected to separate zirconyl from hafnyl chloride, using the Atomic Energy Commission process. Thenceforth, feed material for the plant has been commercial-grade, high-hafnium zirconium tetrachloride.



1 Zirconium Feed Solution
2 Solvent Feed
3 Hafnium Free Zirconium Raffinate
4 Hafnium Laden Solvent Extract
5 Regenerated Solvent
6 CNS Free Zirconium Raffinate
7 Solvent Stripped of Zirconium
8 Scrubbing Acid, H_2SO_4
9 Zirconium Free Hafnium Raffinate
10 Scrubbed Solvent
11 NH_4OH
12 Recovered NH_4CNS
13 Stripping Acid, HCl

Figure 21.

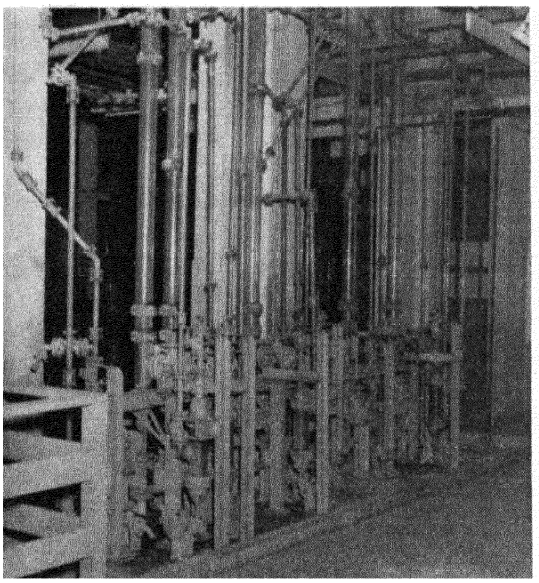


Figure 22. View of base of extraction columns

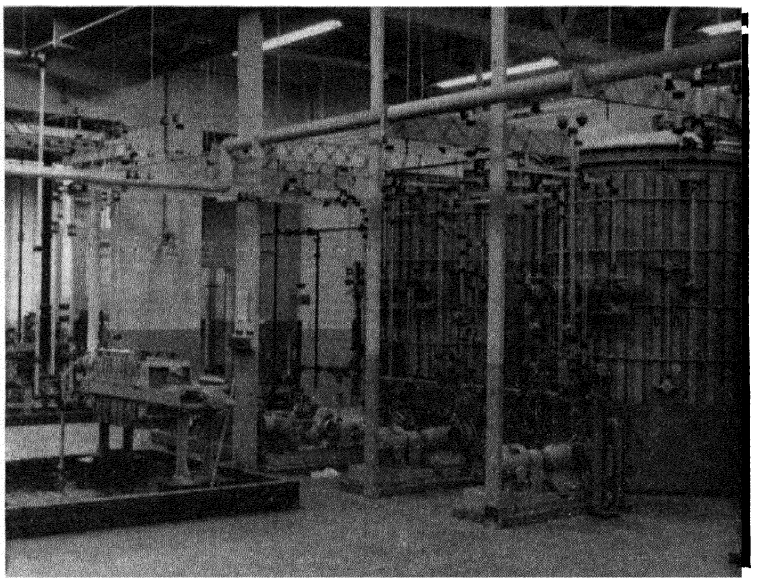


Figure 23. View of storage tanks, pumps, and filters

Improvements in processing and melting were developed. Contaminants were controlled gradually to the extent that metallic impurities and nitrogen were within the limitations expected from zirconium refined by the van Arkel process. Oxygen values approached the same figure. Oxygen is not objectionable from a corrosion standpoint and within limits adds strength advantageously. Consequently, it became evident that the sponge was satisfactory without further treatment and the practice of refining zirconium sponge for use by the Atomic Energy Commission was discontinued in 1952. Attempts to reduce zirconium from zirconium compounds such as carbides or oxide, using modifications of the van Arkel process, have not been successful.

The plant supplied all domestic requirements for low-hafnium zirconium until January, 1954, when a commercial plant began producing the metal. Total zirconium sponge production to January, 1955, has amounted to 1,112,800 pounds. During the year ending June 30, 1954, the unit cost of acceptable low-hafnium zirconium sponge (less interest, depreciation, and taxes) has averaged $9.33 per pound.

Zirconium, melted in a graphite crucible inevitably picks up carbon. Under very favorable conditions, graphite-melted zirconium would be expected to contain at least 0.1 per cent carbon. The development of a water-cooled copper crucible for arc-melted zirconium represented a major improvement in zirconium metallurgy. Semi-permanent electrode tops of tungsten, rhenium, graphite, or high-melting point carbides were a source of contamination particularly if zirconium contained residual occluded volatiles such as chlorides or magnesium. Molten metal splashed over the electrode tip and gradually eroded it into the metal bath. This led to the development of a consumable electrode consisting of a cold-compacted zirconium bar which is melted by the action of the arc to become the feed material to make up an ingot in a water-cooled copper crucible. The arc is contained in an inert gas at atmospheric, or more recently low gas pressure.

The production program was intended to supply low-hafnium zirconium metal at a reasonable cost to the Atomic Energy Commission by utilizing the Kroll process during the interim period between the development of the process and the installation of production capacity by private industry.

The production program by the Bureau of Mines terminated in May, 1955.

The flow sheet, Fig. 20, shows the sequence of intermediate steps in producing reactor grade zirconium by the Bureau of Mines. The steps will be discussed in detail.

SEPARATION OF ZIRCONIUM AND HAFNIUM

Since April, 1952, the Northwest Electrodevelopment Laboratory at Albany, Oregon, has processed zirconium tetrachloride through the purification plant to produce low-hafnium zirconium oxide and low-zirconium hafnium oxide. The hafnium and zirconium oxides produced were processed further in other parts of the plant to ductile sponge metal, using the Kroll process.

Hafnium is separated from zirconium in a complex, liquid-liquid, countercurrent extraction plant. In the system used, hafnium thiocyanate is extracted preferentially in a hexone-thiocyanic acid mixture from an aqueous solution containing zirconium and hafnium. This process was devised at the Y-12 plant of Carbide and Carbon Chemicals Corporation at Oak Ridge, Tennessee during a period of intensive research beginning in May, 1949.

Overholser[47] and Leaders[48] investigated 14 different organics and selected a di-ethyl ether thiocyanate system as being most promising of the group. Further study of the di-ethyl ether system and a rather comprehensive study using hexone as the

extractant was made by Overholser.[49] In a later report covering 5-weeks' work Leaders described the adaptation of mixer-settler apparatus and packed columns to the counter current, continuous, selective extraction of hafnium ions from an aqueous solution by a solution of thiocyanic acid in hexone.

In January, 1950, Leaders[50] summarized the latest improvements in zirconium purification as developed by the Y-12 research, pilot plant, production and engineering groups. Cost estimates were presented for the construction and operation of permanent zirconium purification facilities.

Later work by Leaders,[51] Grimes,[52] Barton,[53] and Waldrop[54] covered the refinement of processing variables using the hexone-thiocyanate system for the separation part of the process and the use of salicylic acid as the organic precipitant in the purification of the products.

Knox[55] made a conclusive study of various materials of construction to determine which materials would resist the combination of hexone and inorganic acids.

Googin[56] presented a revised estimate of the cost of a permanent plant and new operating costs on the substitution of phthalic anhydride for salicylic acid in the purification step.

Ramsey[57, 58] described the complete separation-purification plant equipment, operating costs, and operating conditions.

In April, 1951, the Northwest Electrodevelopment Laboratories at Albany, in cooperation with the Atomic Energy Commission, began construction of a similar plant to supplement the Y-12 production. The Bechtel Corporation completed the building and process design and Bureau of Mines personnel erected the building and installed the equipment. The building was completed in January, 1952 and the plant was equipped and ready for operation in April.

In 1953 the Carborundum Metals Corporation completed a new, integrated zirconium plant near Akron, New York. Their purification plant is essentially the same as the Bureau of Mines facility. With on-stream conditions and production quotas attained, the need for continuation of the Bureau of Mines production plant ceased to exist. The result was closing of the purification plant in January, 1955 and shut down of the balance of facilities scheduled for July 1, 1955.

Feed Preparation (See flow sheet Fig. 21)

Commercial grade zirconium tetrachloride containing 2–3 per cent hafnium is solubilized and fed to the plant as zirconyl chloride. This feed contains hydrochloric acid and ammonium thiocyanate. After adjusting the feed batch to meet these conditions it is filtered into storage tanks (1) and proportioned to the number 1 extraction column.

Extraction System

The extraction system is made up of 4 glass columns (Fig. 22). Feed entering the top of this system passes countercurrent to the thiocyanate-containing methyl-isobutyl ketone which enters the bottom of the system (2). The aqueous solution (raffinate) leaving the system (3) contains only small quantities of hafnium. The organic leaving the extraction columns (4) contains the balance of the hafnium and a substantial quantity of the beginning zirconium.

Thiocyanate Recovery

The raffinate leaving the extraction system is passed countercurrent to fresh or regenerated solvent containing no thiocyanate. The raffinate flows by gravity from the overflow through a polishing press to storage tanks. The solvent flows to the scrubbed solvent tank where it is mixed with scrubbed solvent and pumped to the bottom of the extraction system(2).

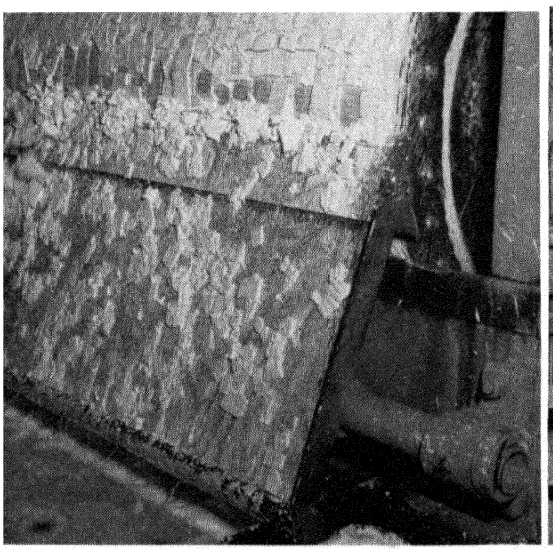


Figure 24. View of rotary filter discharge showing character of zirconium phthalate cake

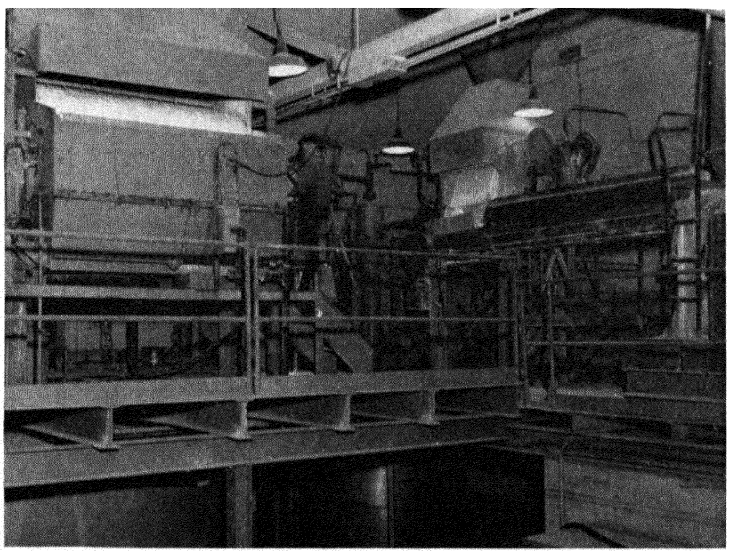


Figure 25. Repulping facilities showing the 3 ft × 6 ft Oliver filter on left and 3 ft × 2 ft Eimco filter on right

Figure 26. Rotary drier and calcining furnace used to convert zirconium hydroxide to oxide

Stripping System

The stripping system is made up of 3 columns. Solvent leaving the extraction system (4) enters the bottom of the first stripper and passes countercurrent to the hydrochloric solution (13) which strips zirconium from the solvent and returns it to the feed pump with essentially the same ratio of hafnium as the beginning feed. The hafnium bearing solvent (7) leaving the last stripper is pumped to the scrubbing column.

Scrubbing System

Scrubbing is accomplished in a column by passing sulfuric acid solution (8) countercurrent to the stripped solvent. Essentially all metal ions are removed in this column so that the hafnium sulfate contains impurities which also are extracted preferentially with the hafnium. These include cadmium, boron, and titanium. The aqueous hafnium sulfate (9) leaving the column passes by gravity through a polishing press to a storage tank. The solvent is returned to the scrubbed solvent storage tank (Fig. 23).

Solvent Regeneration

Scrubbed solvent is contacted with ammonium hydroxide solution (11) in a heat exchanger to remove the CNS present and provide solvent feed for the CNS recovery column. The ammonium thiocyanate (12) thus formed is filtered and held in storage tanks for use in feed make-up.

Zirconium Purification

Raffinate from the extraction plant is stored in tanks for 24 hours until a determination, giving the pounds of zirconium per gallon, has been accomplished. The zirconium in this solution then is precipitated with either di-ammonium phthalate or sulfuric acid.

The di-ammonium phthalate was used as the precipitating agent until very recently when the sulfuric acid precipitation was devised. Both reactions require dilution of the zirconium to 0.1 pound/gallon and both take place most effectively at a pH of 1.4–1.8 and temperatures of 170–195°C. Under these conditions most impurities are left in solution and pass through the filtration system to the sewer. The most troublesome impurity, aluminum, is easily occluded in the cake when the dilution is not correct. The amount of reagents used in either case is given in Table V.

Precipitation is accomplished in a 200-gallon, glass lined, jacketed reactor. Precipitating reagents enter the top of the vessel and leave in a slurry from the bottom through a gravity leg to a 3 ft × 6 ft rubber-covered Eimco rotary vacuum filter. The filter cake shown in Fig. 24 is discharged over a scraper blade to a repulper where 28 per cent ammonium hydroxide is added to promote conversion to zirconium hydroxide. This zirconium hydroxide is pumped underground to the chlorination plant and filtered on a 3 ft × 6 ft wood-decked Oliver rotary vacuum filter shown in Fig. 25 which rejects the ammonium sulfate filtrate through a polishing press to the sewer and discharges the cake to a second repulper where 28 per cent ammonium hydroxide is added.

Drying and Calcining

The endless belt leading to the drier passes under infra-red lamps which serve to warm the zirconium hydroxide cake and lessen its tendency to stick to the walls of the rotary drier.

The drier, which is shown in Fig. 26, is an indirect, electrically fired, rotary shell type, 3 feet in diameter and 30 feet long. There are three zones of heating which are set to 350°, 375°, and 400°C for drying of the sulfate-converted oxide. The discharge falls by gravity to an 18-inch diameter 12-foot long rotary, indirect electrically-fired calciner. The cast "Thermalloy-40" retort is held at 700°C for calcining of the sulfate oxide. The calciner product is accumulated

Table V. Purification of Zirconium by Precipitation

Additions	*Phthalate*	*Sulfate*
Raffinate, 0.7 lb/gal	84	84
Water, gal	200	300
Di-ammonium phthalate, gal	34	—
Conc. sulfuric acid, 33*N*, gal	—	2.2
Ammonia, gal	As required	As required
Temperature, °F	175	190
pH	1.3–1.8	1.2–1.6
Total dilution, lb/gal	0.16	0.15

in 50 gallon open-top drums where it is weighed and sampled, prior to storage in wood-storage tubs outside of the building.

The phthalate-type oxide averaged 71.8 per cent zirconium in a total of 676,583 pounds of oxide product. The sulphate-type oxide contains about 5.0 per cent combined LOI and SO_4 for a conversion factor of 70.4 per cent zirconium.

Process Improvements

The original design in the purification plant has been changed to improve efficiencies and lessen downtime. Many of these changes had to do with piping and flow; some were in the nature of added equipment, such as heat-exchangers and pumps; while still others necessitated searching for corrosion-resistant construction materials. These alterations to the extraction plant improved the recovery of both zirconium and hafnium.

ZIRCONIUM PRODUCTION

Chlorination

Direct chlorination of zirconium oxide was developed on an experimental basis under the research program carried out simultaneously with the expansion of production facilities. In February 1951, plans were made to build a large-scale chlorination unit and the unit was placed in operation in May 1951.

The original unit consisted of two chlorinators, each having a bed diameter of 26 inches, with space provided for a third chlorinator, if needed. Mixing, briquetting, and drying equipment was provided to supply the raw material for the chlorinators. Demands for chloride continued to increase and the third chlorinator was completed in March 1953.

Feed material to the chlorinators is in the form of briquets 1½ inches long by 1 inch wide by ¾ inch thick. The briquets are formed in a briquetting machine, of the Belgian Roll Type, from batch mixes of zirconium oxide, sugar, water and carbon. Figure 27 is a photograph of the briquetting machine. The oxide, as received, is mixed in a ribbon mixer in the ratio of 564 pounds of zirconium oxide to 24 pounds of powdered sugar for 15 minutes. One hundred pounds of carbon is added and the dry ingredients mixed for another 15 minutes. Five gallons of water are added through a perforated pipe along the top of the mixing chamber and the blend mixed for 1½ hours. The batch is discharged into a hopper mounted below the mixer and left to age for about 18 hours.

The batches are conveyed and elevated into the briquetting machine. The pressure with which the material is forced into the rolls is controlled by a paddle type packer mounted above the rolls and powered by a dc variable-speed motor. Soft briquets are broken up and the fines removed through a vibrating screen located below the rolls. These fines are recirculated to the packer through a screw conveyor elevator. Powdered graphite fed onto the rolls keeps the briquets from sticking and also improves the conductivity of the surface of the fresh briquets.

The briquets are dried at 120°C (250°F) in stainless steel trays in a forced-air-type drying oven. Fines are removed from he dried briquets by means of a vibrating screen. Suction lines leading from

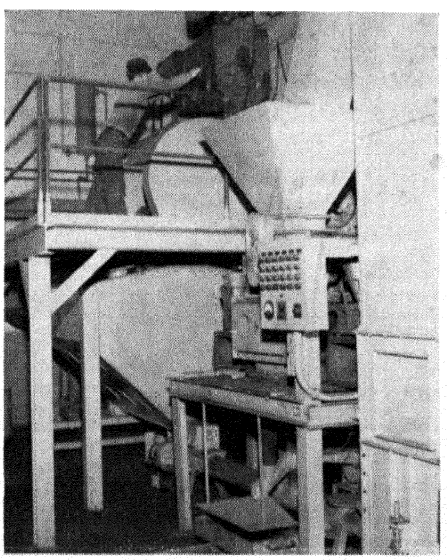


Figure 27. Belgian roll-type briquetting machine

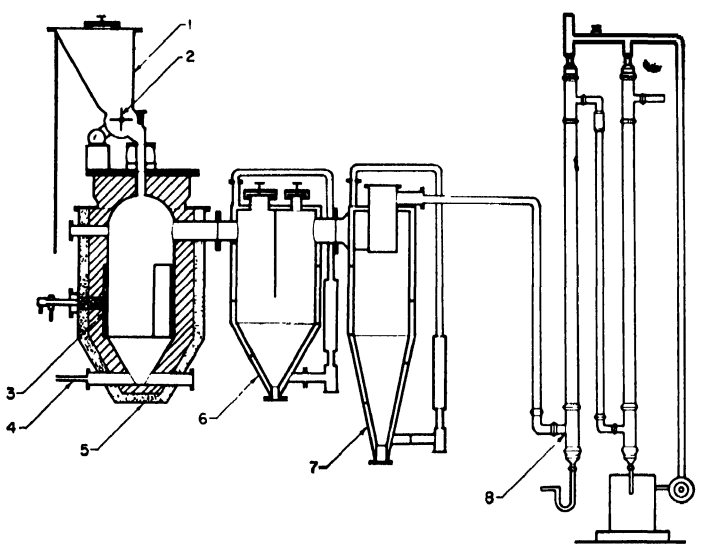


Figure 28. Direct-chlorination unit: (1) feed hopper; (2) feeder; (3) electrode; (4) chlorine inlet; (5) chlorination furnace; (6) condenser; (7) after condenser; (8) scrubbing towers

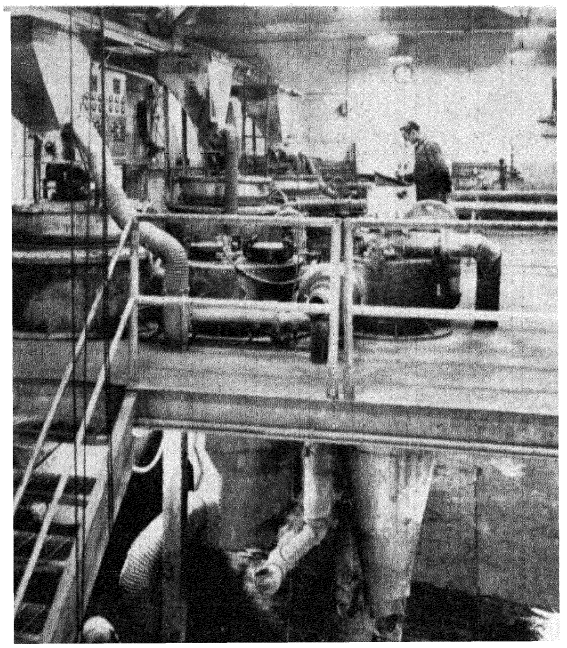


Figure 29. Direct-chlorination unit

the screen to a cyclone separator eliminate the dust hazard and permit recovery of the material lost in the screening operations. All of the fines are recirculated through the briqueting machine.

The design of the chlorination units is shown in Fig. 28 and a photograph of the units is shown in Fig. 29. The electrical power is supplied by three 500 ampere welding transformers, which are connected to auto-transformers adjustable by tap settings to apply 50 or 25 per cent of the voltage to each chlorinator. Under normal operating conditions the voltage and amperage readings are 15 volts and 250 amperes.

Preparatory to the start-up of the chlorinator, either initially or after shutdown for repairs, the chlorinators are charged with dried briquets until the level of the bed is up to the center of the electrodes. Strips of resistor carbon, about 4 inches wide and 2 inches deep are placed from the center of the charges out to each electrode; then more dried briquets are added until the desired depth of charge is obtained. These resistor carbon strips transfer enough heat to the surrounding briquets to cause them to become conductive and the heated area expands until the entire charge is brought to operating temperature is reached, briquets can be added without further addition of resistor carbon strips. During operation, the charge is kept loose and free of voids by periodic packing down through the charging port with an iron rod. Feeding briquets from a sealed hopper into the chlorinator through star valves regulated by clock timers maintains the feed in balance with the rate of chlorination. The hoppers may be filled without interrupting the chlorination by closing a ball valve located just below the star valve. Gaseous chlorine is supplied to each chlorinator through metering valves and a manifold

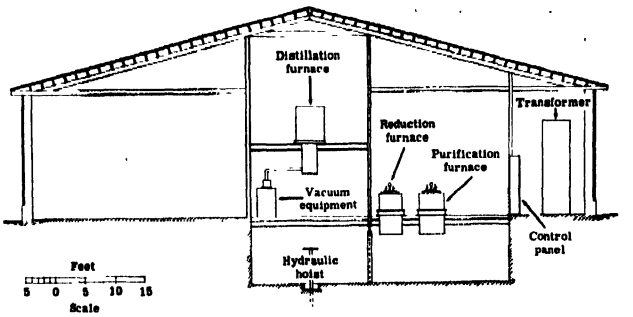


Figure 30. Cross section of zirconium reduction plant

from a chlorine vaporizer. Liquid chlorine is fed to the vaporizer through a manifold connected to several 1-ton containers. A low-pressure diaphragm-protected gauge in each line beyond the metering value indicates the back pressure through the chlorinators, and warns the operator of dangerous conditions arising from restrictions in pipes and equipment.

Chlorinators are operated at a production rate of approximately 50 pounds of zirconium tetrachloride per hour and a bed temperature of 600–800°C. Under these conditions, no top heaters or condenser inlet heaters are necessary to keep the zirconium tetrachloride in the vapor state until it reaches the condenser. The condensers have air vibrators and hammering plates attached for use whenever the product needs to be shaken loose from the sidewalls to expose fresh condensing surfaces. Zirconium tetrachloride dust entrained in the exhaust gases is recovered in second, or after condensers. This entrained dust represents 5 to 7 per cent of the total product. The exhaust gases pass through two 6-inch glass pipe scrubbing towers before venting from the stack to the atmosphere. Both towers are packed with 1-inch Raschig rings to a height of 8 feet.

Waste cooling water plus overflow from the second tower feeds the first tower, and the second tower contains recirculated caustic solution with continuous make-up. Waste water from the towers

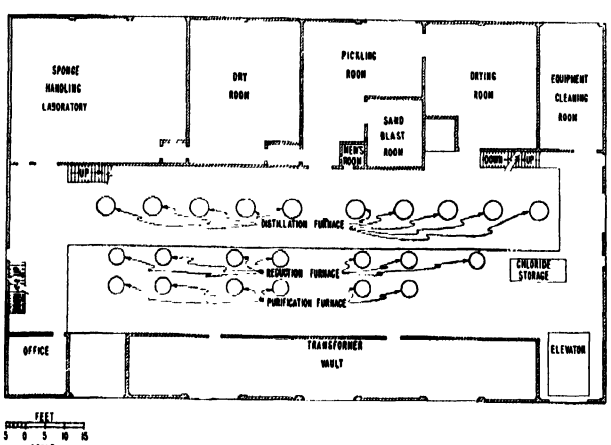
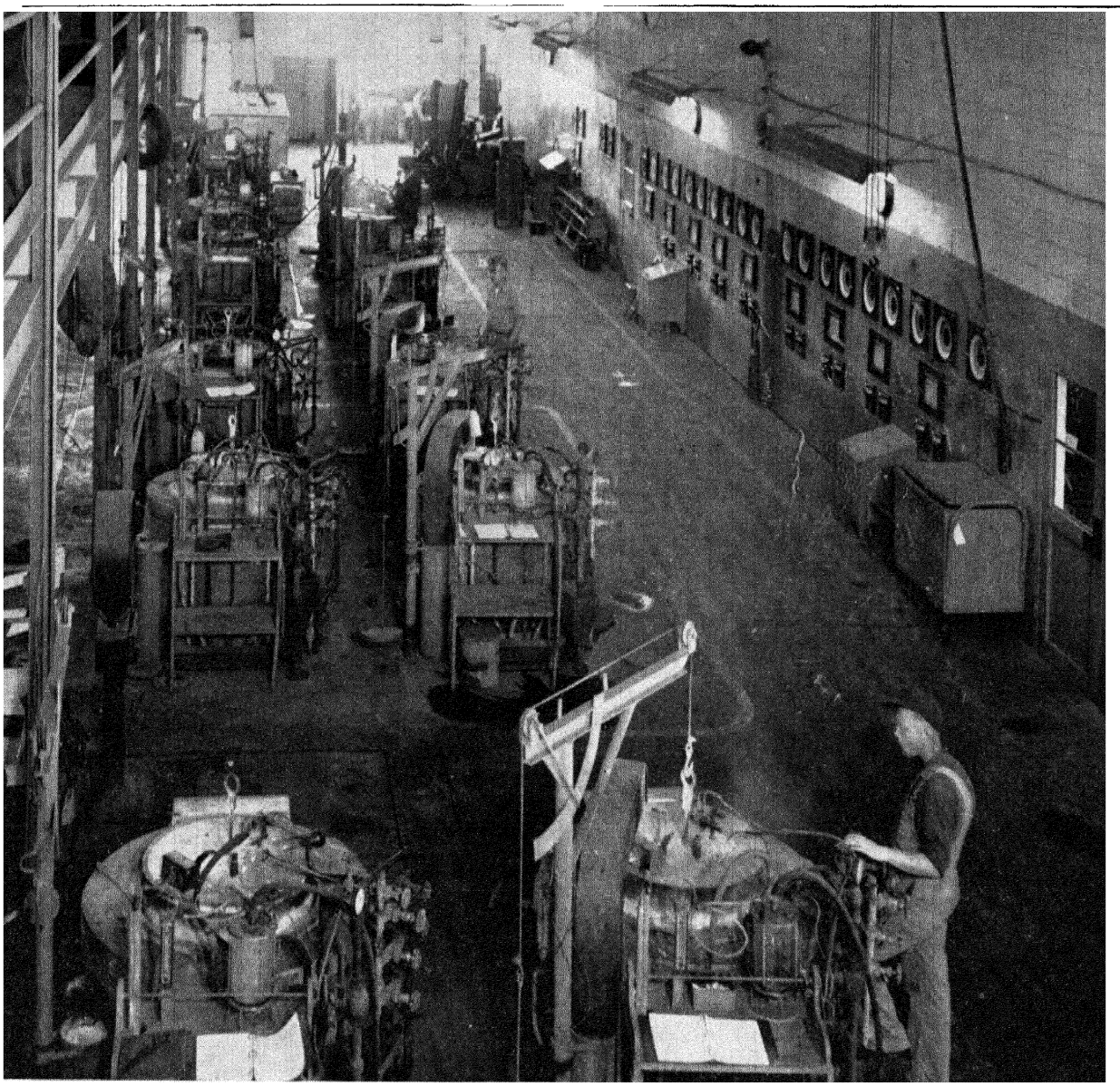


Figure 31. First-floor plan, zirconium-reduction unit



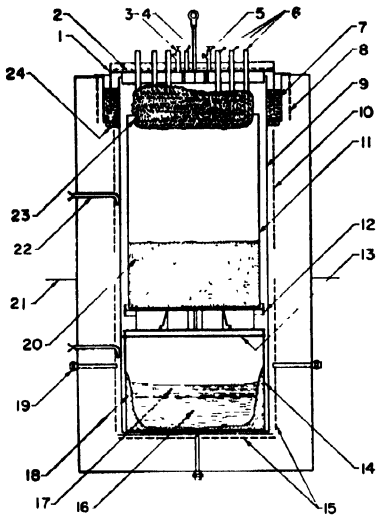
flows through tile drains and a lime pit for neutralization of acid and chlorine before going into the sewer.

Acid fumes from the condenser discharge and clean-out, residue discharge, and briquet charging ports are carried away by suction lines to a spray tower before being blown into the atmosphere..

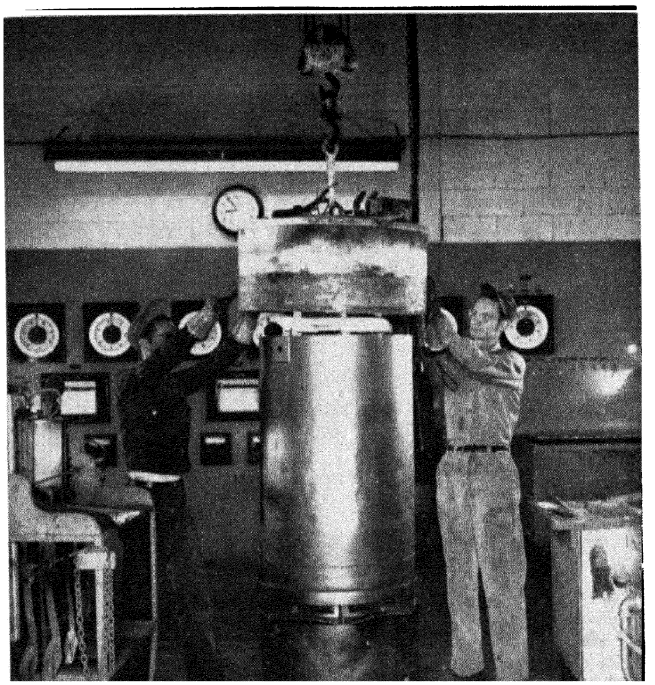
Purification-Reduction

A building 97 feet wide and 150 feet long houses the zirconium reduction unit. The center section has a mezzanine floor on which the distillation furnaces are supported and a basement is located below a portion of the operation floor to provide space for the hydraulic hoists and access to the lower portions of the furnaces extending below floor level. Figure 30 is a cross-section plan of the zirconium reduction plant. The first-floor plan, Fig. 31, shows the layout of the furnaces. The purification-reduction furnaces are arranged in two rows, six in the first row, and seven in the second. The vacuum-distillation retorts are located on the mezzanine floor in the high center section of the building. These retorts are heated by seven "bell" type furnaces, which are moved from one retort to another by means of an electric crane as required in the distillation cycle. Figure 32 is a photograph of the operating floor of the zirconium production unit.

The purification-reduction furnaces are pit-type, with Nichrome resistance elements for heating. The retorts have an inside diameter of 27¾ inches and are 70 inches long and are made of Type 310 stainless steel ¼ inch thick. A trough 2 inches wide by 9 inches deep is welded around the outside circumference of the retort. The top of the furnace rests in the trough which is filled partially with a lead-antimony eutectic alloy (melting point 247°C). When the lead-antimony alloy is molten, the top is free to move and float in the liquid seal during the operating cycle. A stainless steel pipe through which air or water may be circulated is welded to the bottom of the trough and provides the means whereby the lead-alloy seal may be frozen when



gure 33. Assembly of combined purification-reduction furnace:) floating top; (2) top-plate heating element; (3) bleeding valve; l) evacuation tube; (5) gas valve; (6) cooling coils; (7) lead seal; l) lead-seal heating element; (9) retort; (10) middle-zone heating lement; (11) chloride can; (12) reduction baffle; (13) crucible lifting ar; (14) reduction crucible; (15) lower zone heating element; (16) agnesium chloride; (17) magnesium; (18) zirconium; (19) cooling lugs; (20) raw $ZrCl_4$; (21) floor line; (22) thermocouple well; (23) dense $ZrCl_4$; (24) lead-seal cooling coils



baffles, and reduction crucible

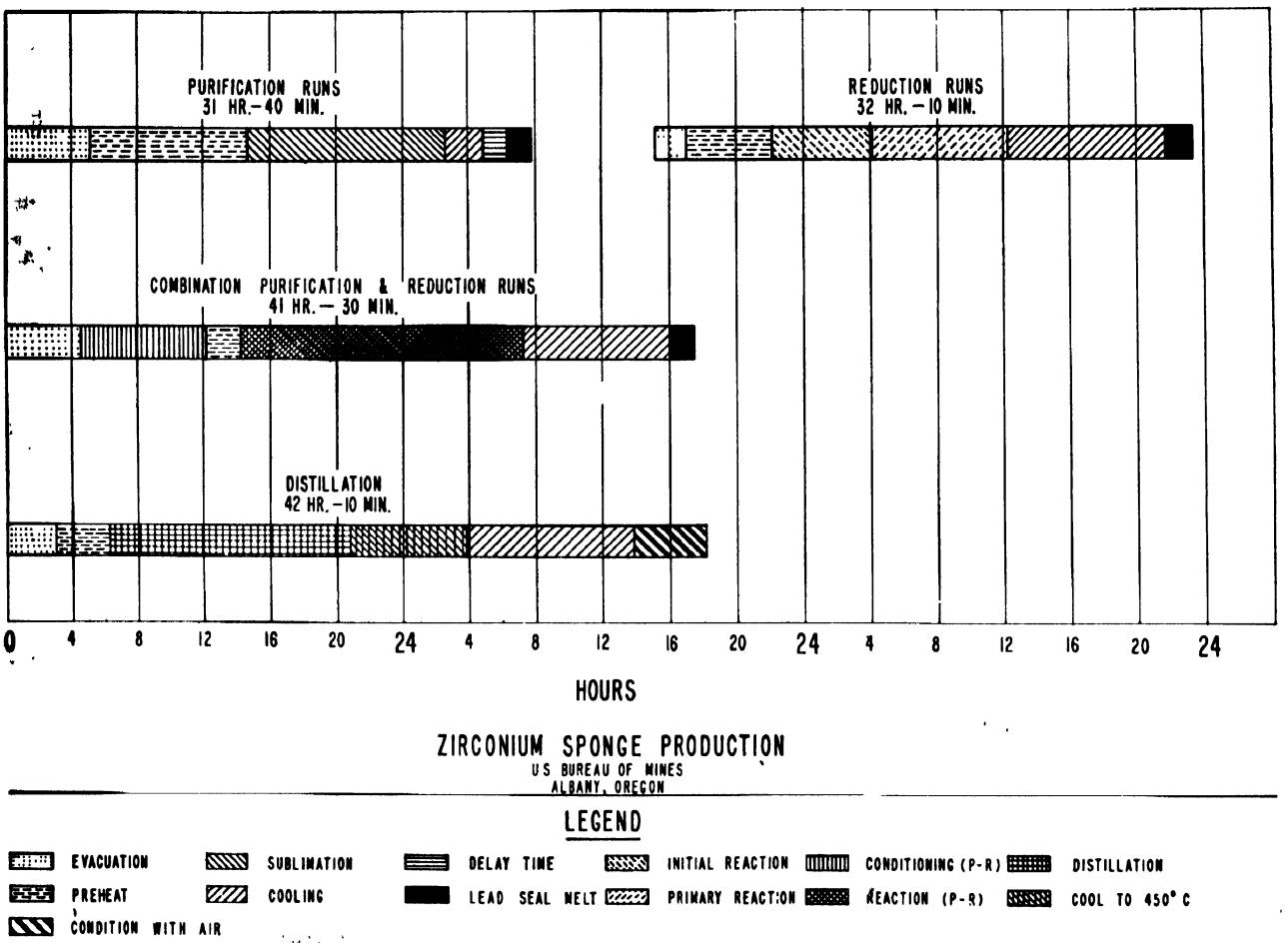


Figure 35. Magnesium reduction process operation schedule

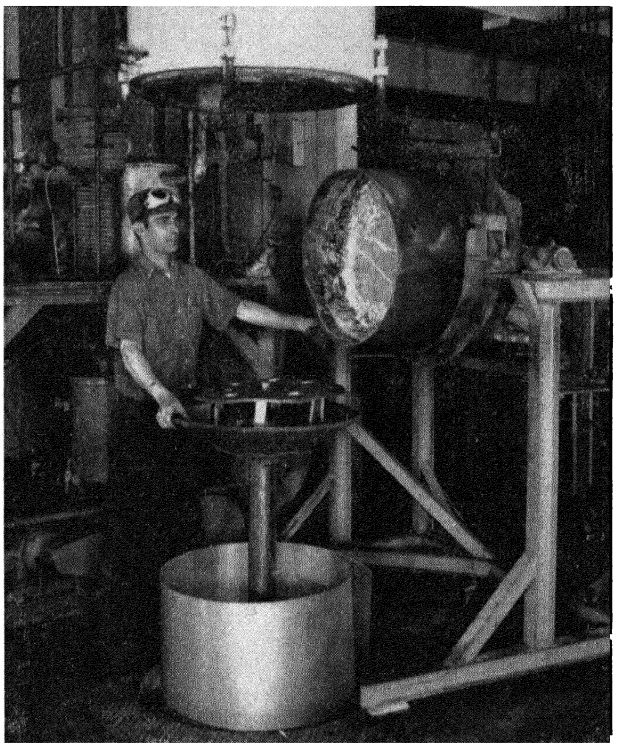


Figure 36. Reduction crucible turned on side to show charge

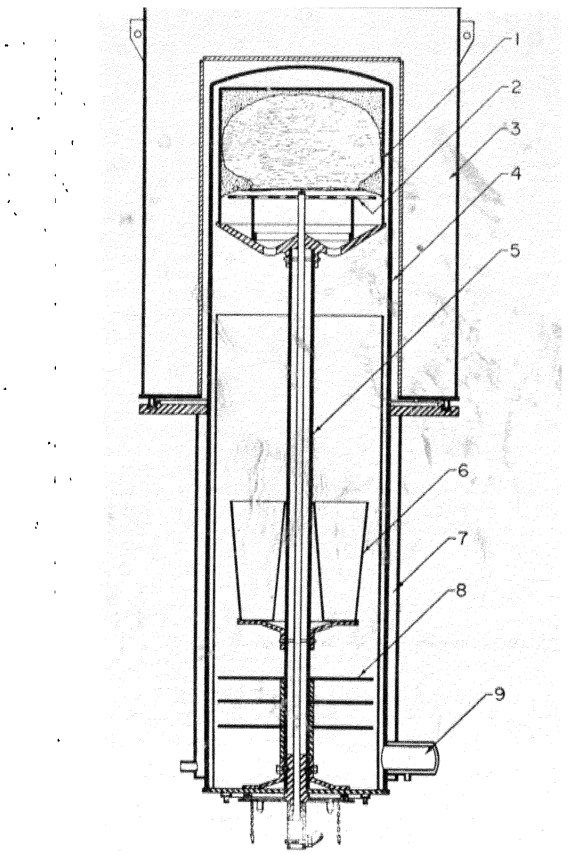


Figure 37. Diagrammatic sketch of distillation furnace: (1) crucible; (2) table; (3) furnace; (4) retort; (5) support column; (6) salt can; (7) water-cooling jacket; (8) baffles; (9) vacuum connection

necessary in the operation of the furnace. Each furnace is equipped with three heating zones; the upper zone located around the lead-alloy seal is rated at 13 kw and extends down the retort for 11 inches; the middle zone heating element, which is 28 inches long, starts about 2 inches below the top heating zone, and has a power rating of 46 kw; the lower heating zone also has a power rating of 46 kw including a 4-kw element in the bottom of the furnace. Furnace tops, which are interchangeable, are equipped with a 5-kw heating element. In normal operations the maximum setting for the floating top heating element and the upper heating zone around the lead-alloy seal is 500°C (932°F). The middle and lower heating zones may be operated as high as 900°C (1650°F).

The heating elements in the floating top and the retort heating zones are provided with thermocouples and individual temperature controlling instruments. Thermocouple wells, welded to the side of the retort, are located in each heating zone, the lower zone having two wells on opposite sides of the retort. A multi-point recorder is used to record continuously the furnace operating temperatures and furnishes a visible indication of the operating temperature in each zone for the operator as well as serving as a check on the automatic temperature controllers.

Each furnace is used for both the purification and reduction steps. Both the reduction crucible and the zirconium chloride container are loaded in the furnace before the start of the run. A short baffle is used, which rests on the top of the reduction crucible and supports the chloride container. The cooling

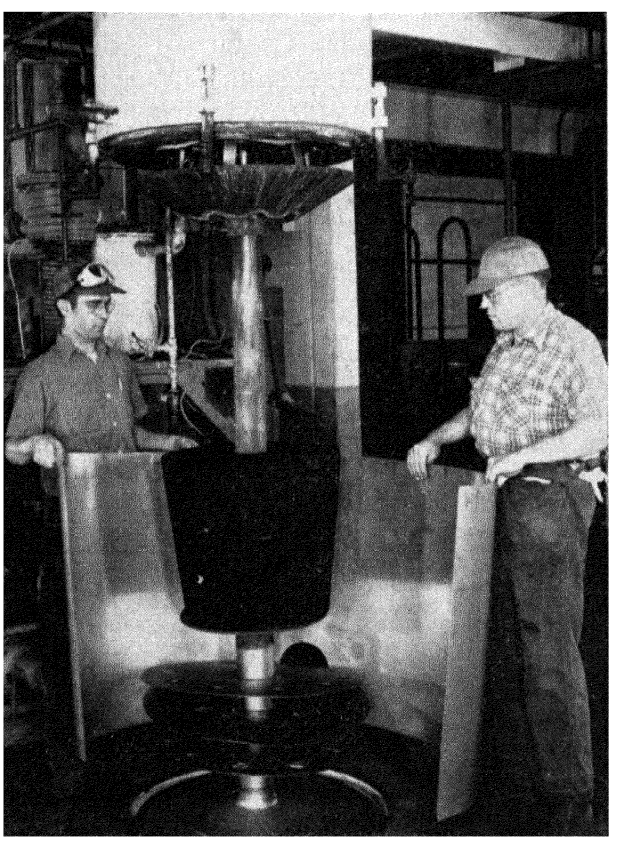


Figure 38. Furnace equipment for vacuum distillation

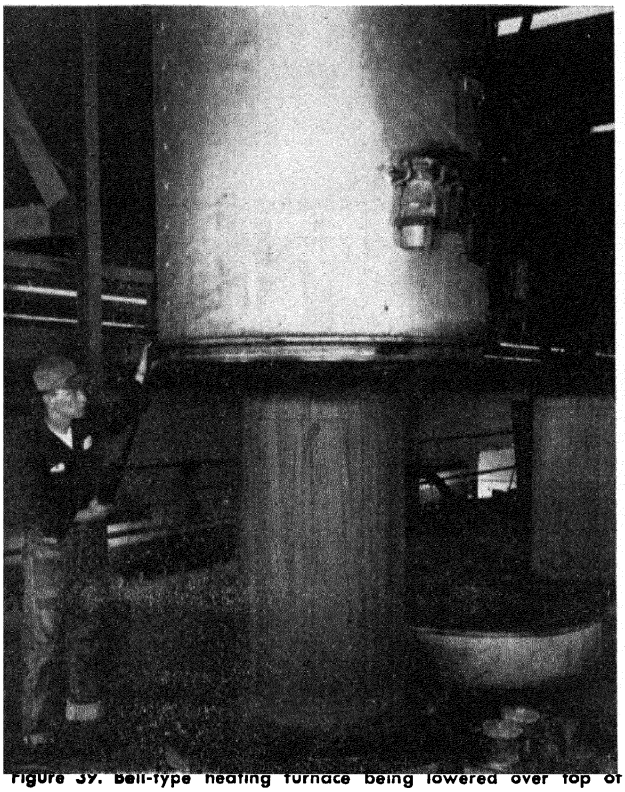


Figure 39. Bell-type heating furnace being lowered over top of distillation retort

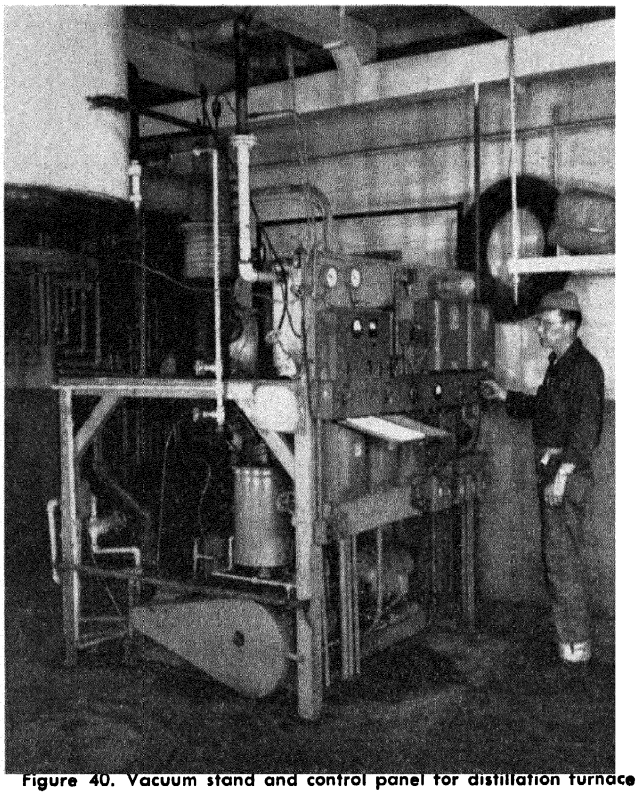


Figure 40. Vacuum stand and control panel for distillation furnace

coils in the floating tops are 9 inches in length. The equipment is shown in Figs. 33 and 34.

Standardized charges of magnesium and zirconium tetrachloride are used in order to maintain the proper excess of magnesium over the stoichiometric amount needed for the reduction. The furnace is charged by placing a reduction crucible of Type 430 stainless steel containing 120 pounds of magnesium-metal pigs in the bottom of the retort and placing the baffle on the top of it. The weight of zirconium tetrachloride remaining on the condensing coils from the previous run must be determined, because this becomes part of the furnace charge. The zirconium tetrachloride charged into the choride container is regulated so that the total chloride content is between 515 and 525 pounds. The chloride container and its contents are placed in the furnace on top of the baffle and the floating top is lowered into position in the lead-alloy seal. Water is circulated through the cooling coils under the seal until the lead-alloy solidifies. As soon as the seal is frozen, the temperature controllers on the lower, middle, and floating top elements are set at 300°C (570°F) and evacuation is started. Water aspirators are used for the evacuation. In order to remove the gaseous impurities from the charge, three evacuations are made. The furnace is refilled with helium between each evacuation and a two-hour heat soak is included between the first filling with helium and the second evacuation. Helium is used as the flushing gas.

After the furnace has been filled with helium for the third time, cooling of the lead-alloy seal is stopped and the temperature controller for the lead-alloy seal is set at 550°C in order to melt the lead-alloy seal rapidly and free the floating top. Controllers for the top plate, middle zone, and lower zone heating elements are set at 350°C (600°F). During the time the lead-alloy seal is melting the furnace is "bled" at 10-minute intervals. The temperature controllers for the top plate, middle zone, and lower zone elements are left at the 350°C setting for two hours, and are then raised 10°C every ½ hour until a maximum setting of 450°C (840°F) has been reached. "Bleeding" of the furnace is continued until the operation has been repeated 100 times.

Experience has indicated that this procedure is required to remove volatile impurities from the zirconium tetrachloride charge. However, as a result of the operation the ratio of zirconium tetrachloride vapor to helium in the furnace atmosphere is too high for control of the initial reaction of the reduction. The desired ratio is arrived at as follows.

The middle-zone heating elements are shut off, the lower-zone controller set at 825°C (1515°F) and the temperature controllers for the top plate and lead-alloy seal heating elements are set at 500°C. Cooling air is circulated through the chloride condensing coils to regulate the bleeding intervals to 5 minutes. One half-hour after the lower-zone temperture controller has been set at 825°C, helium is added to the furnace, through a flow meter, at the rate of 28 cubic inches per minute for 2 hours. "Bleeding" of the furnace is discontinued while helium is being added and the amount of air circulated through the chloride condensing coil is regulated to maintain the floating top in its normal operating position.

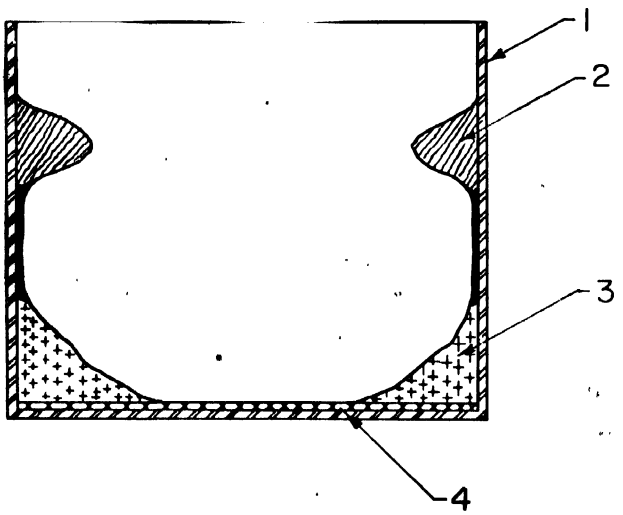


Figure 41. Sponge distribution in crucible: (1) 430 chrome steel crucible (2) type C sponge; (3) type A sponge; (4) type B sponge

The reaction usually begins soon after the addition of the helium has been completed. The temperature of the middle zone is increased, as necessary, to maintain a normal pressure in the furnace and keep the top floating.

The reaction is controlled in his stage to furnish an optimum ratio of concentration of zirconium tetrachloride vapor to helium. The operator allows the reaction to proceed as rapidly as possible without exceeding a recorded lower-zone temperature of 875°C (1605°F). After the start of the reaction, the furnace is "bled" every half-hour. As the rate of reaction decreases, the lower zone temperature drops. When the temperature falls below 850°C in the lower zone, the "bleeding" rate is increased to about 6 or 10 times per hour and the lower zone temperature controller is set to keep the recorded temperature above 850°C.

The combination purification-reduction procedure carries the reaction to completion. The reduction cycle is complete when all the zirconium tetrachloride has been sublimed from the chloride container. Individual runs may terminate within 18 hours after the lower zone temperature controller was set to 825°C.

A sharp pressure drop in the furnace is an indication that the zirconium tetrachloride supply is exhausted. At this time, helium is added to maintain the furnace pressure and the middle-zone temperature is raised to 650°C (1200°F). Any zirconium tetrachloride that may have condensed in the cooler regions of the upper part of the furnace is volatilized and reacted at the higher temperature.

At the conclusion of the reduction, the heat to the furnace is turned off and cooling water circulated in the coil below the lead-alloy seal. A slight positive pressure of helium is maintained in the furnace during the cooling period. In order to increase the rate of cooling, air is blown into the space between the retort and the furnace elements. When the recorded temperature of the lower zone has fallen

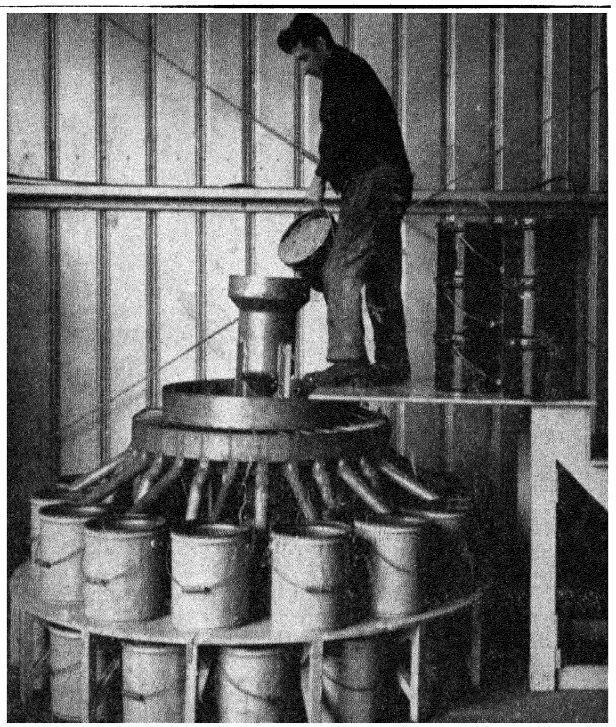


Figure 42. Zirconium-sponge blender

to 150°C (300°F) the furnace may be opened. The lead-alloy seal is melted and the top, baffles, and crucible are removed. The surface of the contents of the crucible is cleaned of any exposed sponge or other reaction byproducts and the crucible either transferred to a distillation retort or to a vacuum-tight storage container to be held until a distillation retort is available.

The time necessary for completion of a reduction cycle depends upon the rate of reaction that can be maintained by the operator. A typical operating schedule is shown in Fig. 35.

Vacuum Distillation

At the end of a run, the crucible contains magnesium chloride and excess magnesium metal in addi-

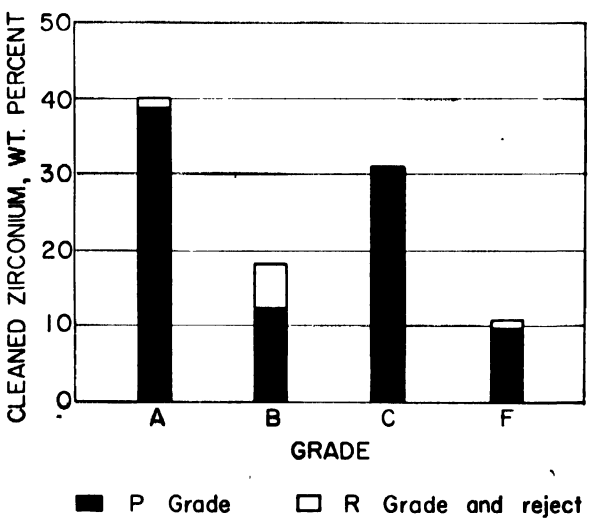
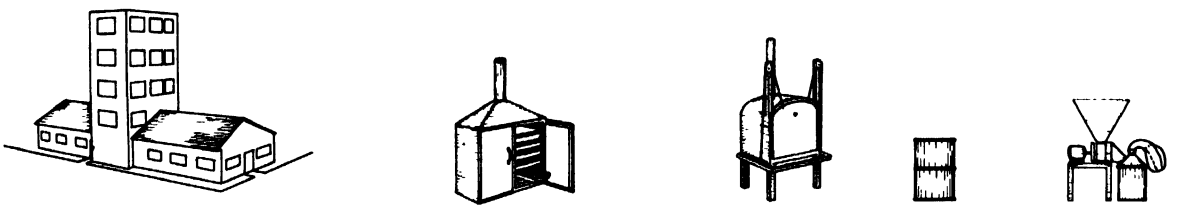
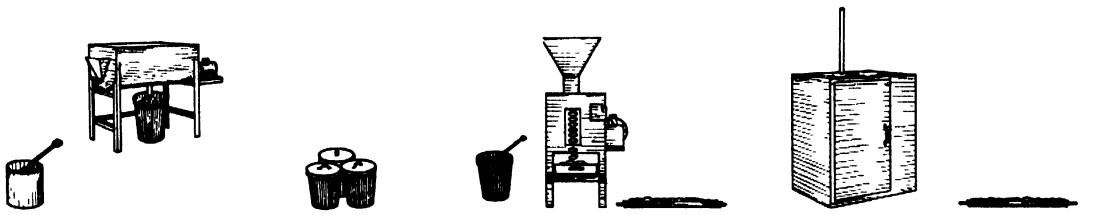
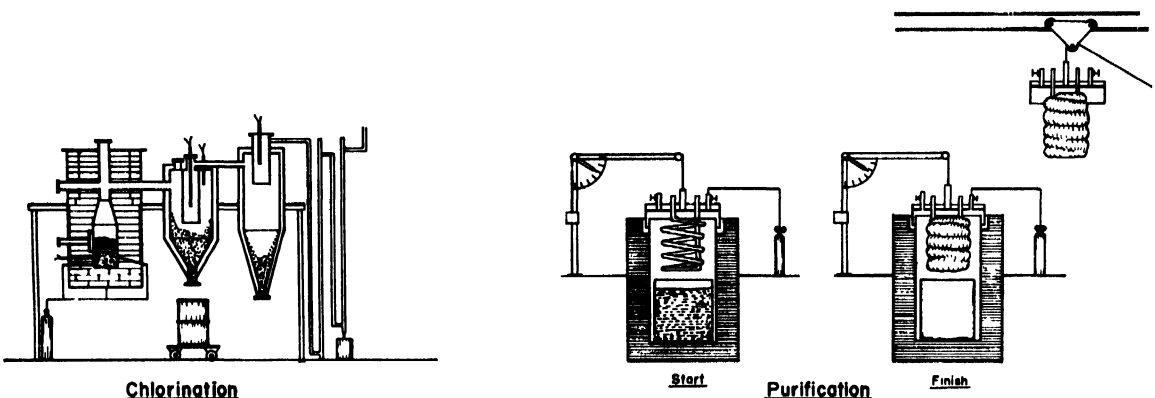
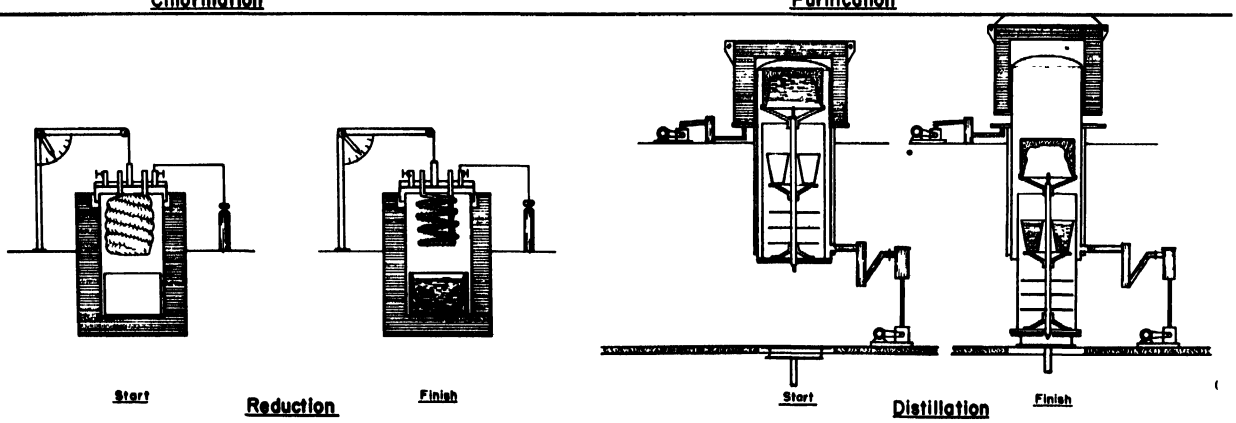


Figure 43. Weight-percent by grade of total cleaned zirconium sponge. (1130 runs; 69,905.30 kg)









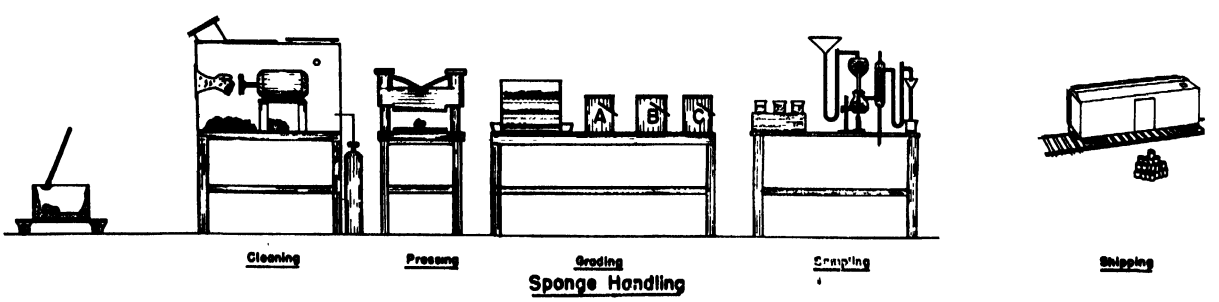


Figure 44. Flowsheet, hafnium production

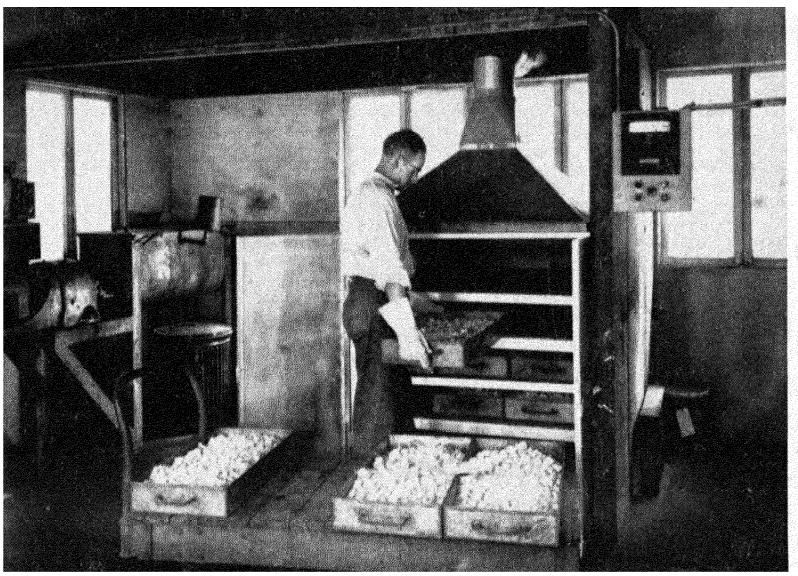


Figure 45. Multiple deck electric drying oven

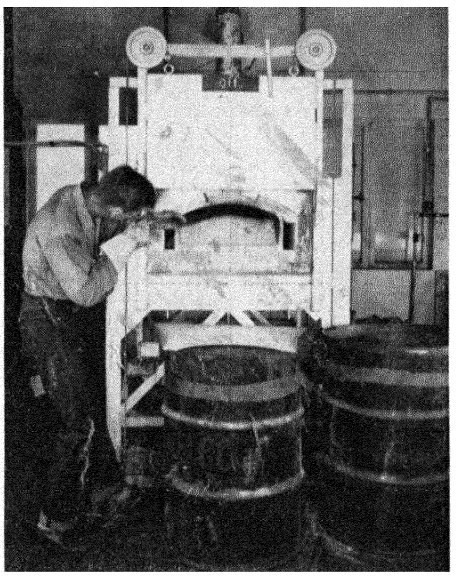


Figure 46. Calcining is done in a muffle furnace

tion to the reduced sponge. Figure 36 shows a crucible at the end of a run. The magnesium chloride and excess magnesium are separated from the reaction mass by heating the crucible and its contents in an inverted position in an evacuated retort. Details of the vacuum retort are shown in the diagrammatic sketch, Fig. 37. The top of the retort is heated by a bell-type resistance furnace and the lower portion of the retort is enclosed in a water-cooled jacket. The upper portion, which is exposed to the heat of the furnace, is made of Type 316 stainless steel ½ inch thick, and the lower portion is fabricated from mild steel. The entire unit is supported by a heavy steel flange upon which the furnace rests during the heating cycle. A recessed rubber gasket is provided in the flange which permits a vacuum-tight seal to be made between the furnace, or hot top, and the flange.

The retort is loaded and unloaded by use of a hydraulic ram, installed in the basement floor. The equipment used inside the retort consists of a 4-inch steel support column, 3 baffles, salt can, crucible support and sponge support table. All these items, which are shown in Fig. 38, are made of Type 302 stainless steel. In preparation for a distillation run, the retort cover is fastened on the ram top and the other equipment fastened to the cover. The crucible is placed in an inverted position on the crucible support, and the sponge support table is set in position beneath the crucible to support the sponge, which otherwise might drop down as the magnesium chloride is distilled from the reaction mass. Enclosing the lower portion of the assembly is a thin, stainless-steel shield which serves as a condensing surface to collect the magnesium chloride distilled from the crucible. A thin, stainless steel well is inserted through a hole in the center of the retort cover and extends upward through the hollow support column to a position just above the sponge support table. It is necessary to use a vacuum-tight seal where the well passes through the retort cover. A thermocouple in this well records the temperature inside of the crucible. Another thermocouple located on the inside of the furnace, near the heating elements, is used to control the furnace heating.

The rubber sealing gasket on the retort cover is cleaned and lightly greased before the cover is raised into position and clamped. The ram top is detached, the ram lowered, and the recording thermocouple inserted in the well. In Fig. 39 the furnace is shown ready to be lowered over the retort.

Each distillation retort is equipped with the necessary vacuum equipment which is mounted on a stand beside the retort on the operating floor level. Figure 40 shows the vacuum stand and control panel for one distillation unit. Two vacuum systems are employed, one to evacuate the interior of the retort and the other to evacuate the space between the furnace and the exterior of the retort. This is necessary to balance the pressure and prevent collapse of the hot retort during operation. A mechanical pump is used to evacuate the space between the heating elements and the retort; and the normal pressure obtained is below 1 mm of mercury. An oil diffusion pump backed by a mechanical pump is used to evacuate the inside of the retort. Drying towers containing trays filled with P_2O_5 are placed in the vacuum lines between the pumps and the rest of the vacuum system and serve to protect the mechanical pumps from water vapor. This system is capable of reducing the pressure in the retort to the order of 0.05 micron. Regular Bourdon-type gauges are used in both systems for visual observation of the progress of the evacuation in the early stages. A closed-end mercury manometer is used to check the final vacuum in the space between the retort and the furnace and the other system is equipped with an ionization discharge-type vacuum

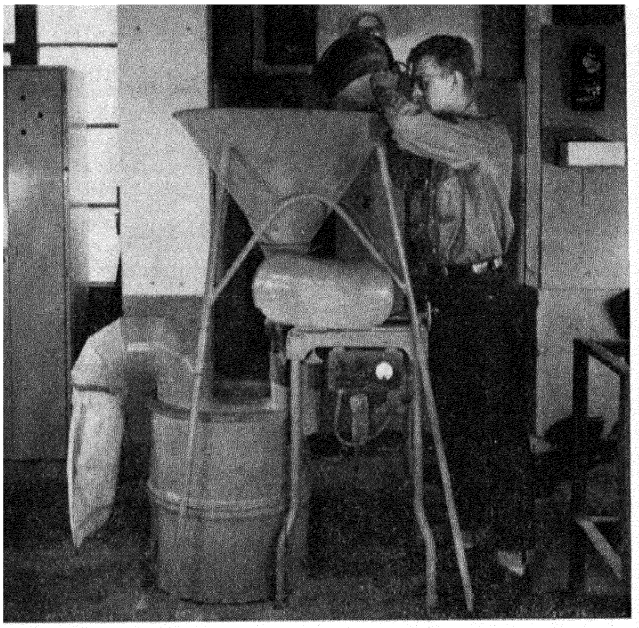


Figure 47. Cooled calcine being fed to a hammer mill

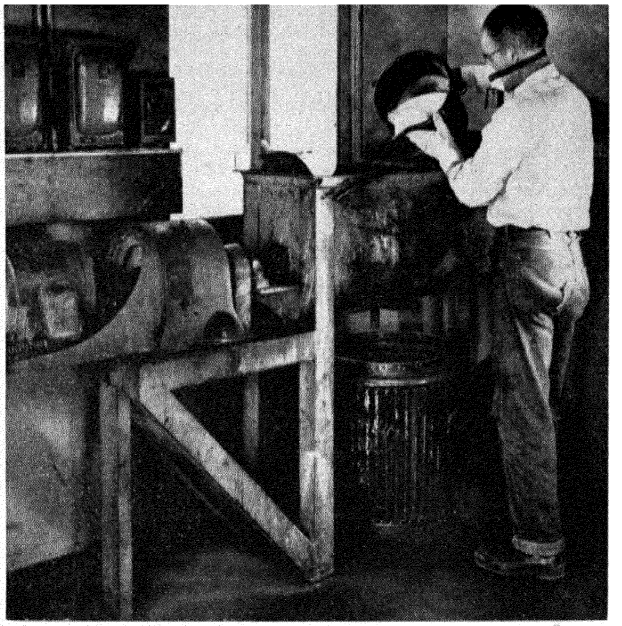
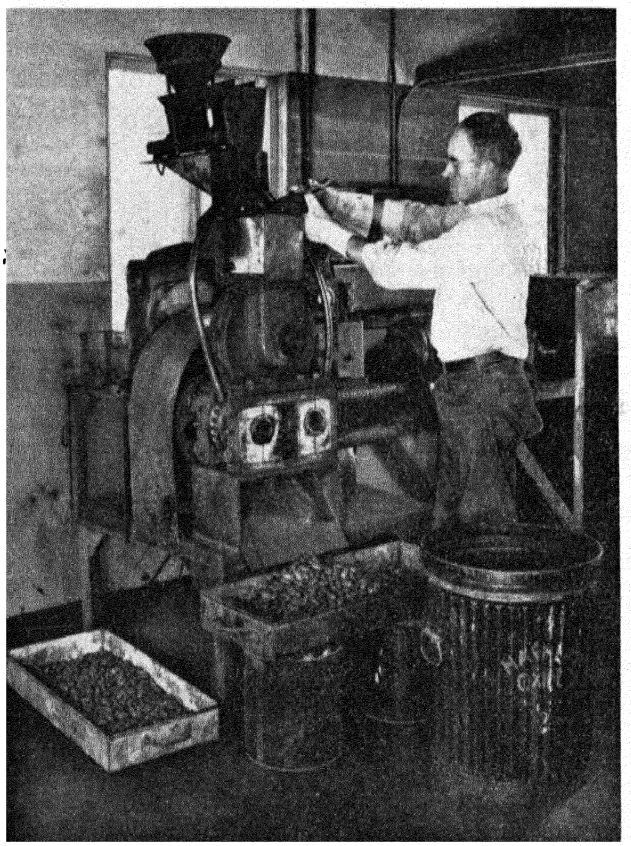
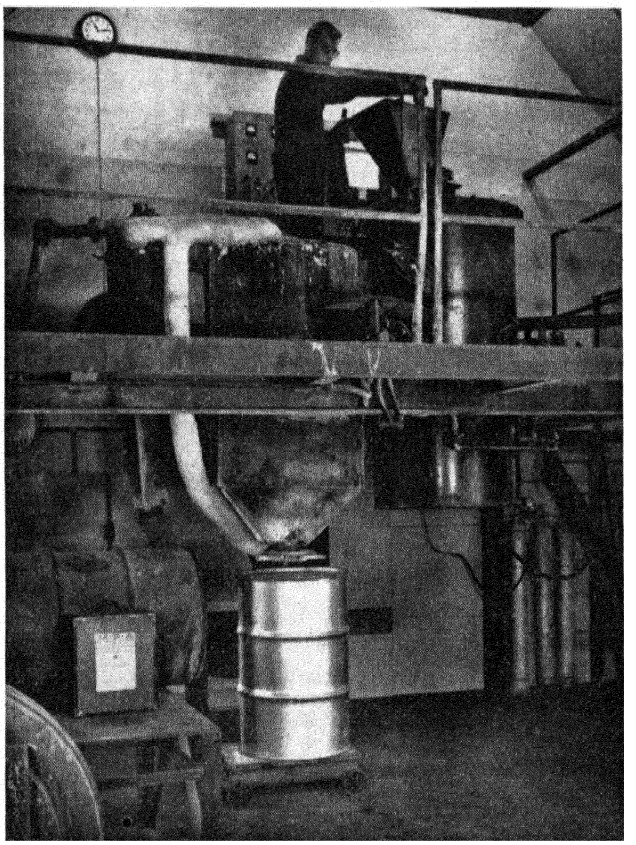


Figure 48. The oxide and sucrose are ribbon mixed





gauge and a thermocouple-type vacuum gauge for determination of operating pressure within the retort.

A small, portable vacuum pump is used to evacuate the retort to a few millimeters of mercury before the regular pump is started. Use of this portable pump in this manner materially reduces the maintenance of the regular vacuum equipment.

When the pressure within the retort has been reduced to 20 microns, the vacuum valves are closed and a leak-rate check is made. If the leak-rate is acceptable, the valves are opened and the heating furnace is lowered into position on top of the retort and a vacuum tight seal obtained between the flange and the furnace. Evacuation of the space between the retort and the furnace is then begun, and the furnace temperature control is set at 960°C (1780°F). The furnace temperature is maintained at this level for 14 hours. Then the power is turned

off and the furnace removed, after filling the space between the furnace and the retort with dry air. After removal of the hot top, the furnace is cooled in the air for approximately a half-hour when a water spray is placed on the top to speed cooling. During this time a vacuum is maintained on the inside of the retort. When the recorded temperature inside the retort falls to 600°C (1110°F), the vacuum pumps are turned off and the retort is filled with helium to increase the cooling rate. Cooling of the furnace is continued until the recorded temperature reaches 37.5°C. The retort is evacuated again and filled with dry air. Another evacuation is made and the retort refilled with room air, which is left in the furnace for 1 hour to condition the exposed surface of the sponge. This conditioning of the freshly distilled sponge is necessary to minimize the danger of burning. After the conditioning period is over, the retort is evacuated again and refilled with helium. The equipment is dis-assembled, the crucible removed, and transferred to the sponge handling unit. The salt can is emptied and the remainder of the equipment washed and dried in preparation for another distillation cycle.

Sponge Handling

Since the reduction of zirconium is a batch process, variations in the sponge produced from run to run can be expected and probably no two batches have ever been identical. Differences are noted from batch to batch in the physical appearance of the sponge and its relative location in the crucible. However, the distribution falls into a general pattern as shown in Fig. 41.

Type *A* sponge generally accounts for about 35 per cent of the weight of sponge from a reduction and is dense material appearing in massive chunks. It is lower in magnesium and chloride contamination than the other types.

Type *B* sponge represents about 20 per cent of the total weight of the sponge. It is deposited usually as a plate about ⅜-inch thick near the bottom of the crucible and is believed to be formed during the initial reaction of the reduction. It normally is high in iron, nitrogen, and metallic impurities except magnesium.

Type *C* sponge is a true sponge, being very light and porous. About 35 per cent of the total weight of the sponge falls into this classification. Because this type is porous in structure, considerable magnesium and chlorine are entrapped in the pores, and the impurity level of these elements is high. However, this type of sponge is lowest in other impurities and redistillation will reduce the contamination by magnesium and chlorine to satisfactory levels.

Type *F* sponge designates material from a run in which no clear-cut distinction can be made and the sponge cannot be graded into the usual types. All of the sponge from such a reduction is classified as Type *F* and processed together.

Approximately 10 per cent of the total raw sponge is rejected during cleaning and sorting because of appearance and high impurity. Normally this is returned to the chlorinator for recycling in the process.

When the crucible containing the sponge is received from the reduction unit, the contents are removed by using pry bars and a 50-ton frame-type air press and chisels. The *C* sponge usually can be removed without breaking, but the *A* and *B* sponge must be broken up before removal. Any black deposit adhering to the *A* and *B* sponge is removed by buffing before crushing. Pieces of sponge too large to handle in the crusher are cut with a chisel in a 200-ton hydraulic press. Zirconium in the sponge state can be ignited easily during handling and the crucible is flooded with argon gas during the removal operation to minimize the fire hazard. Sponge can be shipped safely in a steel pail mounted in a wooden box, provided the air in the pail is replaced by a noble gas.

The sponge is reduced to minus ⅜ inch in a gyratory crusher and passed over a vibrating screen to remove the fines. Each grade of sponge from every run is handled separately and sampled for chemical and spectrographic analyses for a number of contaminating elements. To prepare the samples for analysis, split samples of about three pounds each are briquetted in a 4-inch diameter die at 200-tons pressure. Each briquet is drilled with a multiple-point ⅜-inch drillhead (six drills) and the shavings are used as samples for chemical and spectrographic tests. Typical analyses for three sponge samples are shown in Table VI.

Table VI. Typical Analyses (ppm)

	Sponge		
	A	*B*	*C*
	Chemical		
Fe	500	600	300
N_2	40	70	40
Mg	200	200	900
Cl_2	200	150	700
	Spectrographic		
Al	30	90	25
Mn	35	55	15
Si	40	150	35
Ti	25	25	25
Mo	*20	*20	*20
Cr	65	85	45
Cu	15	15	20
Ni	13	12	12
Pb	40	55	25
Sn	10	10	10
Zn	*50	*50	*50
B	0.2	0.2	0.2
Hf	67	63	73
Cd	*0.5	*0.5	*0.5
As	*50	*50	*50
P	*100	*100	*100
V	*20	*20	*20
Bi	*1	*1	*1
Co	*20	*20	*20
Sb	*50	*50	*50
Ag	*0.5	*0.5	*0.5
Be	*1	*1	*1

*Less than.

In order to obtain a large uniform batch of material for melting, small lots of sponge are blended together to form a composite of 2000 pounds or more. A specially constructed blender for this purpose is shown in Fig. 42. Sponge lots are poured, one at a time, into a hopper above a rotating vibrating feeder, which discharges into a circular splitter of thirty compartments. Any split portion, representing one-thirtieth of the blend, can be mixed further in a stainless steel double cone mixer, if desired.

Distribution of Impurity Elements

As the zirconium sponge is removed from the crucible in the sponge handling room it is classified into one of the several types of sponge on the basis of its appearance and location in the reduction crucible. This is purely an arbitrary separation, based on past experience and knowledge concerning the sponge quality. Each type of sponge from an individual run is weighed and stored separately pending chemical and spectrographic analysis for impurities. Analyses for nitrogen, magnesium, and chlorine are made by chemical methods and the concentrations of the remaining impurity elements are determined spectrographically. Since November 12, 1953, a Quantometer has been used for spectrographic determinations. The analytical information obtained for each type of sponge for individual runs is filed on punched cards. The analysis card shows the run number; grade of sponge; weight in kilograms; chemical analyses in parts per million for nitrogen, magnesium and chlorine; and spectrographic analyses in parts per million for aluminum, copper, lead, chromium, iron, manganese, silicon, boron and hafnium. Cards covering a specific block of production runs may be selected from the files, sorted, and tabulated by conventional punched card techniques to give the desired information concerning the distribution of the impurity elements in the various grades of sponge.

The results of a tabulation of 1130 combination purification-reduction runs and 107 redistillation runs of *C* sponge produced during the period between November 10, 1953 and June 30, 1954 are summarized in Table VII. The quantity of sponge under study was 69,905 kilograms and represented the entire regular production over the period indicated. Average analysis figures given in the table are not weighted averages in the strict sense but are very nearly so, since the weights of individual batches vary only over a narrow range. Fig. 43 is a graphical representation of a portion of Table VII.

Tabulations were made for each grade of sponge to show the total weight in each type which would meet the following batch impurity limits for nitrogen, iron, silicon, and aluminum for *P* and *R* grade sponge.

P Grade:	Nitrogen	150 ppm
	Iron	4000 ppm
	Silicon	200 ppm
	Aluminum	100 ppm
R Grade:	Nitrogen	400 ppm
	Iron	4000 ppm
	Silicon	>200 ppm
	Aluminum	300 ppm
Reject:	Nitrogen	>400 ppm
	Iron	>4000 ppm
	Aluminum	>300 ppm

No sorting of the cards was made on the basis of the other impurity elements since very little difficulty is encountered in meeting *P* grade specifica-

Table VII. Weight Distribution and Average Analyses By Grade and Specification Limits for Iron, Nitrogen, Silicon, and Aluminum*

	Weight % of grade	*Weight % of total*	*Average Analysis, ppm*									
			Fe	N_2	*Mg*	*Al*	*Cu*	*Pb*	*Cr*	*Mn*	*Si*	*B*
A Sponge	100	40.0										
P Grade	96.8	38.7	509	35	203	27	15	42	66	34	41	0.2
R Grade	2.0	0.8	505	208	314	35	15	40	53	35	105	0.2
Reject	1.2	0.5	11,361	304	1.146	42	32	66	42	131	45	0.2
B Sponge	100	18.1										
P Grade	68.2	12.3	619	61	193	69	15	51	84	52	130	0.2
R Grade	29.3	5.3	647	94	176	150	14	59	89	58	180	0.2
Reject	2.5	0.5	1628	649	421	99	18	95	60	58	167	0.2
C Sponge	100	31.1										
P Grade	100	31.1	288	38	207	26	18	23	43	15	35	0.2
R Grade												
Reject												
F Spouge	100	10.8										
P Grade	88.0	9.5	359	55	997	41	15	59	43	38	64	0.2
R Grade	11.3	1.2	342	192	1232	69	14	85	34	36	71	0.2
Reject	0.7	0.1	300	885	4600	40	20	65	40	43	75	0.2

* Sorted to *P*, *R*, and Reject on basis of batch limits for Fe, N_2, Si, and Al.
P Grade = Fe 4000 ppm or less; N_2 150 ppm or less, Al 100 ppm or less, Si 200 ppm or less.
R Grade = N_2 > 150 ppm but 400 ppm or less and/or Al>100 ppm but 300 ppm or less and/or Si >200 ppm.
Reject = N_2 >150 ppm but 400 ppm or less and/or >300 ppm.

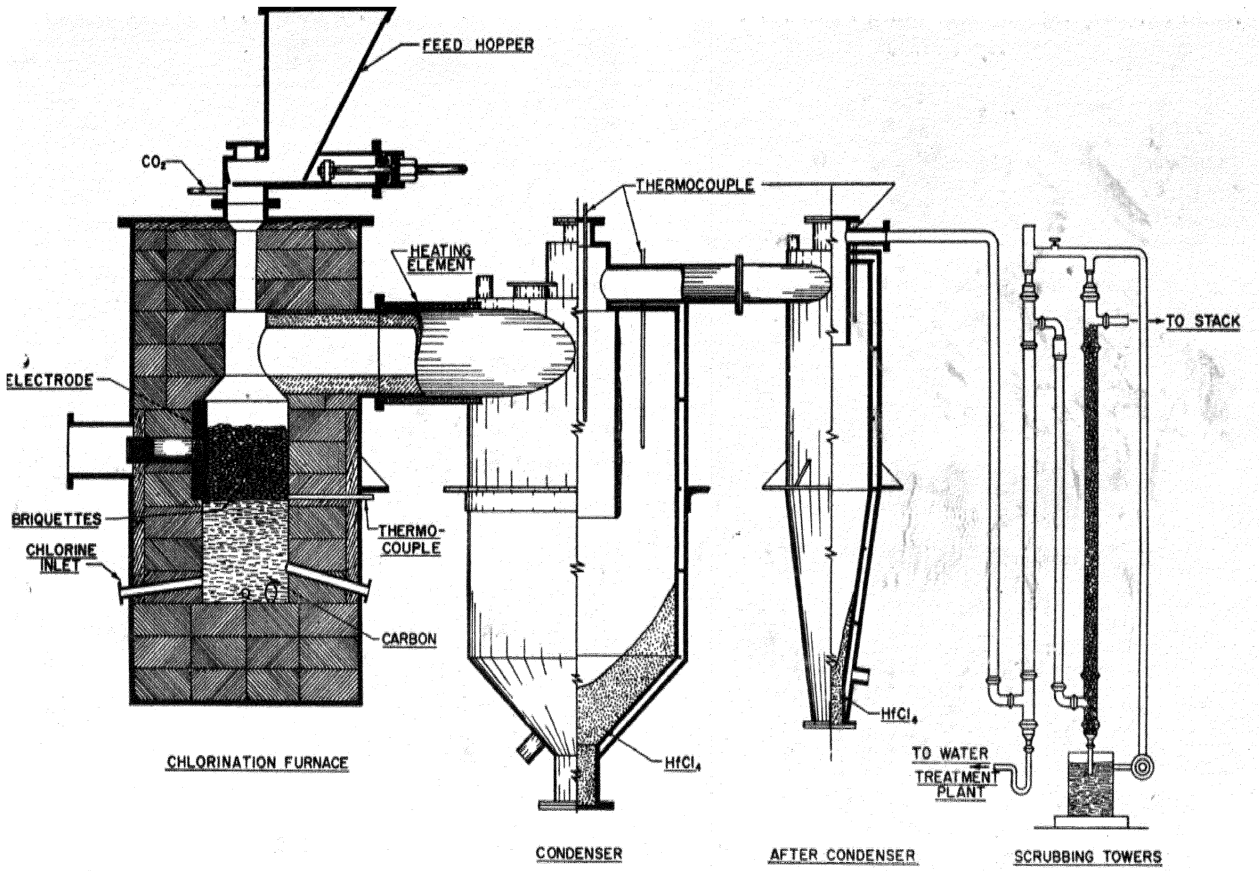


Figure 51. Hafnium chlorination unit

Magnesium content of the sponge can be reduced by redistillation, therefore, if other impurity elements are present in quantities below *P* specification limits, sponge having magnesium contamination in excess of 1000 parts per million is redistilled. All *C* grade sponge is redistilled. The percentage of each grade of sponge requiring redistillation is shown in Table VIII.

Cards for each type of sponge then were recombined, sorted, and separate tabulations made in increasing order of concentration for iron, nitrogen, silicon, and aluminum. Calculations were made from these tabulations to determine the cumulative weight per cent of each type of sponge containing a given amount or less of a specific contaminating element. These data were plotted as the maximum contamination curve. Similar calculations were made for each element studied to determine the theoretical average quantity of residual impurity if all of a particular grade of zirconium with less than a given amount of contamination were blended together. This information was plotted as the average contamination curve. The maximum contamination curve for iron, for cleaned *B* sponge shows that about 95 per cent of this grade sponge contains 1000 parts per million or less of iron. If all of the cleaned *B* sponge containing 1000 parts per million or less of iron were blended thoroughly, the blend theoretically would contain about 530 parts per million of iron.

Contamination of the sponge by any one impurity maximum limits of concentration for more than one element results in a cumulative effect upon the amount of material rejected. An example selected from the maximum contamination curves for cleaned *B* sponge serves as an illustration of this cumulative effect. The maximum limit of 4000 parts per million of iron for an individual batch of sponge permits utilization of 99.7 per cent of the cleaned sponge, a limit of 150 parts per million of nitrogen permits utilization of about 92 per cent, a limit of 100 parts per million of aluminum permits utilization of about 80 per cent, and a limit of 200 parts per million of silicon permits utilization of about 88.7 per cent. These same maximum limits for the four elements, when applied together, permit utilization of only 68 per cent of the total cleaned *B* sponge.

If the distribution of impurities in the cleaned sponge were assumed to be completely random, then the percentage of sponge that theoretically would

Table VIII. Weight Per Cent of Each Grade Sponge Requiring Redistillation

Grade	*% of grade to P units**	*% of P units (Mg >1000 ppm)*	*% of grade to redistillation*
A	96.8	2.6	2.5
B	68.2	3.2	2.2
C†	100	—	100
F	88.0	26.3	23.1

*Sorted on basis of batch limits for Fe, N_2, Al, and Si.
†All *C* sponge is redistilled as a routine procedure.

Table IX. Drying and Calcining Data for Hafnium Hydroxide

Product	Weight, pounds	Per cent moisture	Per cent moisture removed
Filter cake	11,194	80	
Oven dried cake	3247	30	89
Calcine	2262	0	11

meet specifications would be the product of each of the above percentage factors, or 65.1. Since this theoretical figure is lower than the actual yield figure of 68 per cent, some relationship in the occurrence of two or more of these impurities may be indicated.

Most of the de-grading of the sponge during the period covered by this survey was due to excessive contamination of the sponge by aluminum and silicon and to a lesser extent by nitrogen. Since both silicon and aluminum are present in the magnesium used in the reduction, it is logical to suspect a correlation between the amounts of these impurity elements found in the final sponge. Similarly, some degree of interrelationship between chromium and iron contamination levels in the sponge may exist as a result of attack upon the chromium-iron crucible.

Statistical surveys such as these are of decided importance in properly evaluating the effect of changes in equipment or operating techniques which might affect the final quality of the sponge produced.

PRODUCTION OF HAFNIUN

In the production of hafnium metal, modifications in the process have taken the form of alterations or

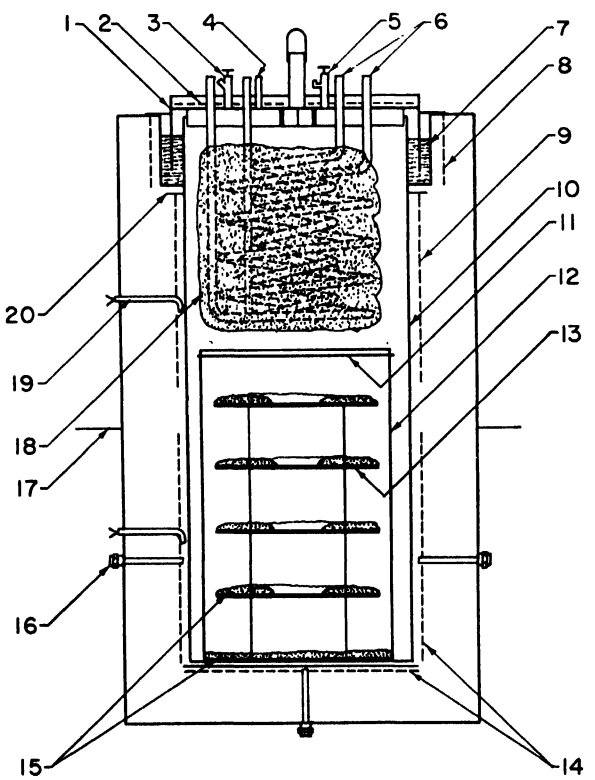


Figure 52. Cross-section of the purification furnace

Table X. Screen Analysis, Hafnium Oxide

Product	Screen size	Weight, per cent
HfO_2	+35	3.6
	35/100	13.8
	100/200	24.3
	−200	58.3
		100.0

changes of a partial character, of equipment, procedures and materials. Exercise of extreme care throughout the process has been attained more easily by these modifications, which have made for a relatively trouble-free operation.

The production of hafnium (Fig. 44), as developed at the Northwest Electrodevelopment Laboratory of the Bureau of Mines, Albany, Oregon, consists of the following steps: (1) separation of hafnium compounds from zirconium ores; (2) converting the hafnium to the oxide; (3) direct chlorination of hafnium oxide; (4) purification of hafnium tetrachloride; (5) reduction of refined hafnium tetrachloride with magnesium metal; (6) removal of magnesium chloride (formed in the reduction process) and the excess magnesium from the hafnium by treatment in a vacuum distillation step; and (7) cleaning and crushing of the sponge in preparation for further treatment.

Separation of Hafnium Compounds from Zirconium Ores and Converting to the Oxide

Commercial grade zirconium tetrachloride is treated by a liquid-liquid separation process to remove hafnium and the other impurities. The process yields purified hafnium hydroxide, which is dried and calcined to hafnium oxide. A multiple deck electric drying oven (Fig. 45) operating at 175°C dries trays of the hafnium hydroxide filter cake in 24 to 36 hours. Calcining is done in a muffle furnace at 800°C (Fig. 46) with little or no hand rabbling so that dust losses are negligible.

Table IX gives the loss on ignition for this step.

The cooled calcine is fed to a hammer mill, Fig. 47, which discharges to a cyclone separator coupled to a bag collector. Dust losses are considered negligible. Screen analysis of the pulverized product is shown in Table X.

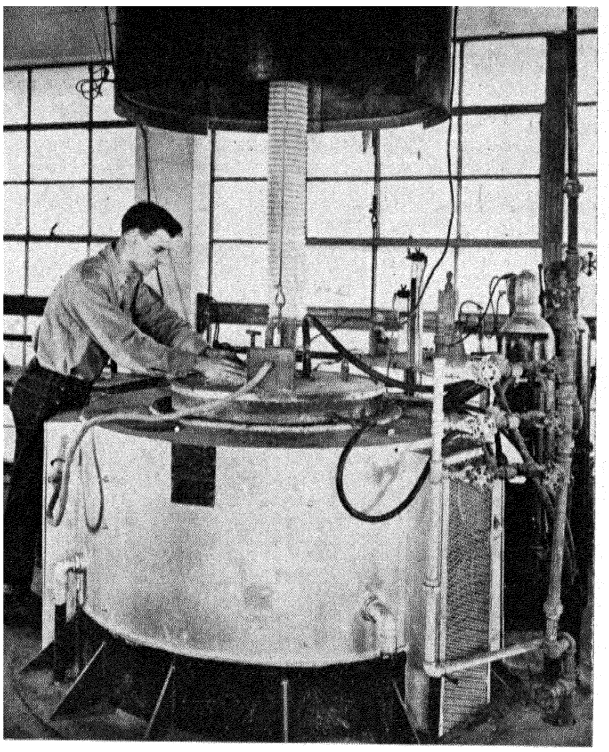
Analysis, by chemical and spectrographic methods, of the calcine and later products, is given in Table XI.

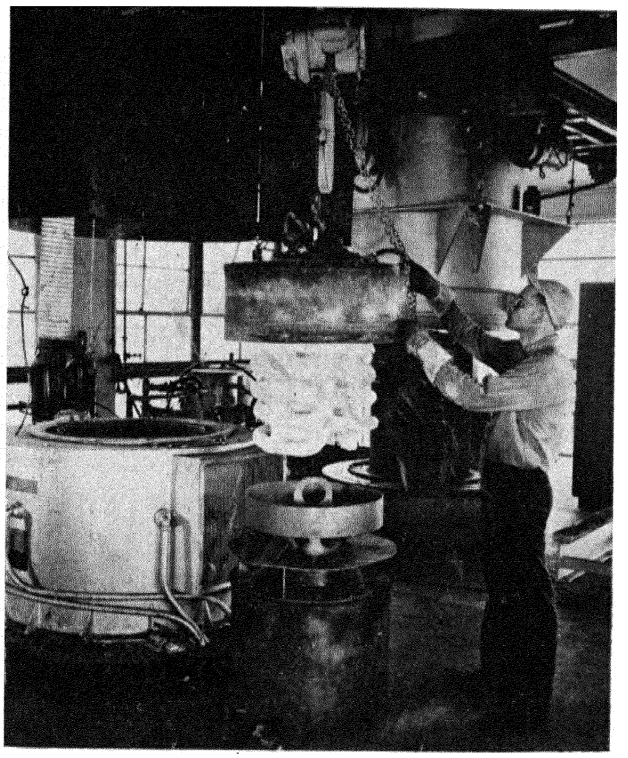
Briquets for chlorinator feed are made from a mix containing 85.5 per cent calcined hafnium oxide, 9.5 per cent carbon in the form of channel

Table XI. Impurities in Hafnium Products and By-products*

	Al	Fe	Si	Zr
Calcined HfO_2	100	2200–4100	1000	0.3–2.2%;
Raw chloride	80	2100–4400	50	Avg. 1.18%
Dense chloride	50	1300–2100	30	
Oxide residue	500	1.6%–7.1%	500	
Vapor phase	500	0.9%–3.8%	50–100	

*Parts per million except where given in percentage.





black, and 5.0 per cent sucrose. This mixture takes into account that the oxide has an average hafnia content of 98.82 per cent, the chief impurity being zirconium. The channel black contains approximately 91 per cent fixed carbon and 9 per cent volatile matter. The oxide and sucrose are ribbon mixed (Fig. 48), 1.4 liters of water per 100 pounds of dry mix is added, and the carbon is blended into the damp mix. This mix is aged for four hours to permit the moisture to diffuse, and then briquetted in Belgian rolls (Fig. 49). The Belgian rolls form a dense, hard briquet, which retains its shape well in the chlorinator bed. Briquets are dried for 72 hours at 150°C.

Direct Chlorination of Hafnium Oxide

The chlorinator (Figs. 50 and 51) is essentially the same as that described[59] for the production of anhydrous zirconium tetrachloride by direct chlorination of a zirconium oxide-carbon mixture in a silica-brick-lined vertical shaft pilot-model chlorinator. The mild steel shell is lined with silica brick to form a vertical shaft, with an inside diameter of 12 inches for a height of 22 inches. Three graphite plates 6 inches wide by 12 inches high and 2 inches thick are imbedded in the lining at 120 degree intervals on the same horizontal plane, to serve as electrodes. Three-phase power is supplied by three modified welding machines. On the primary side there is 480 v, 3-phase, 60 cycle; and the tap arrangement makes it possible to draw the power from the secondary at 17 volts–600 amp, 34 volts–300 amp, 51 volts–200 amp, or 68 volts–200 amp.

The shaft above the top of the electrodes is reduced in cross section to 4 inches. Two charging ports are provided at the top, one for initial charging and one for the sealed-hopper-type feeder used during the run. If it is necessary to bar down the charge during the run, the initial charging port is

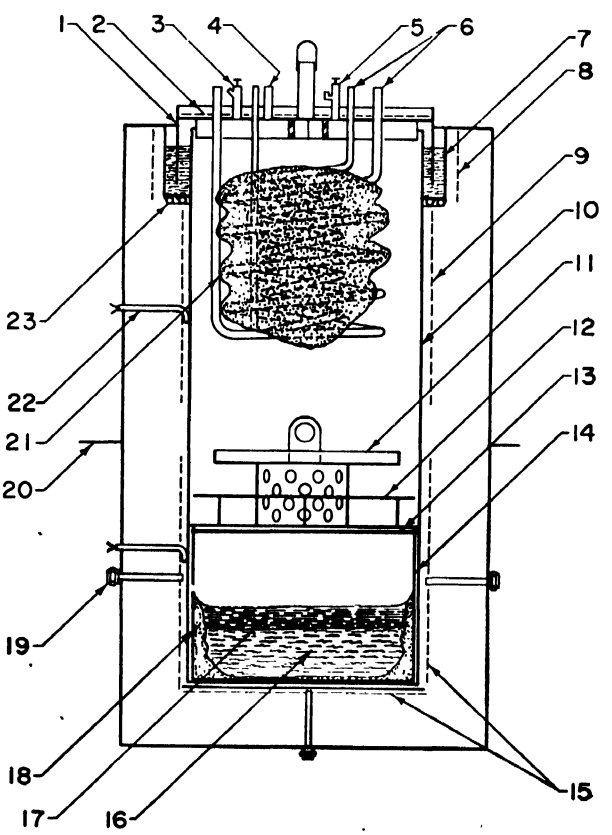


Figure 55. Assembly of reduction furnace

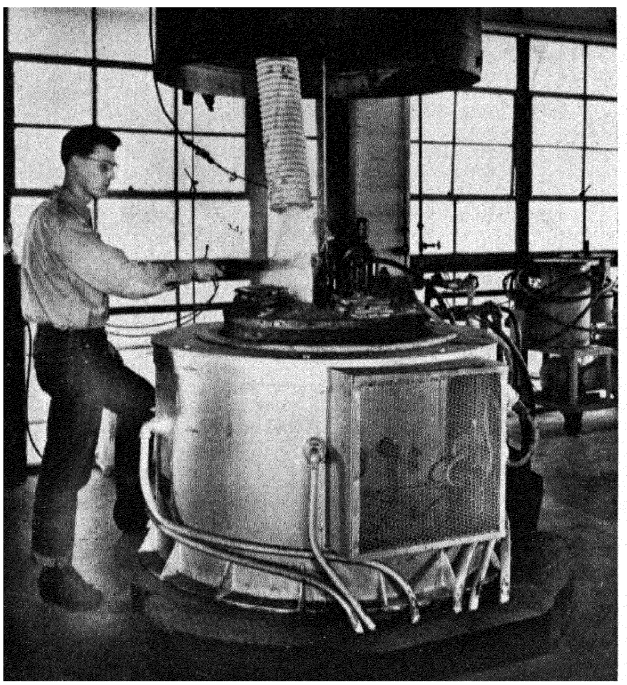


Figure 56. The furnace is bled

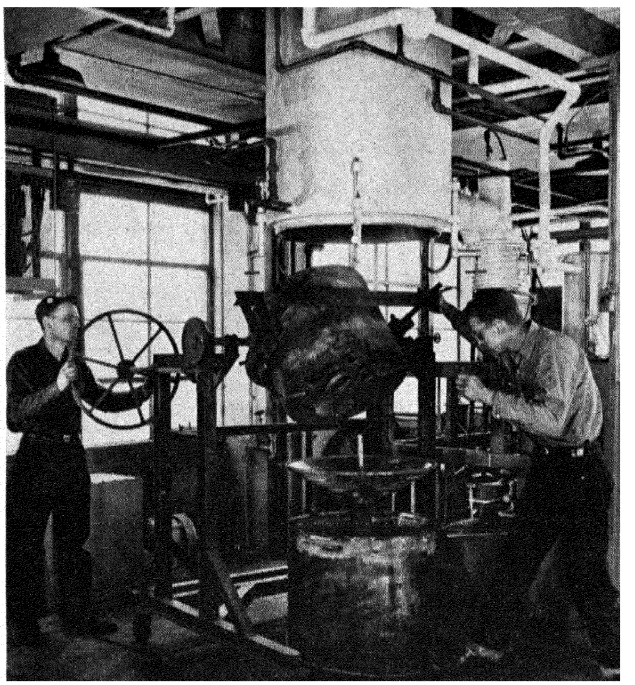


Figure 58. Self-locking table in the crucible

used to admit the bar. The chloride discharge pipe is a graphite tube 6 inches inside diameter with walls 1½ inches thick, the whole being covered with a nickel tube from the chlorinator to the condenser. A 500-watt insulated heating element wrapped over the nickel tube gives adequate heat at this point to prevent condensation of the chloride.

Chlorine gas is preheated by passing it through a coil of helically wound seamless steel tubing which is immersed in a vat of hot water. The chlorine enters the chlorination chamber at four different elevations at or near the three electrodes but, in all cases, below them. This has been found advantageous in securing even chlorination throughout the charge. One or more inlets may be open at any one time. Change of inlet is indicated at any time the three recording thermocouples indicate a cold spot in the bed with a corresponding hot spot to be found near the chlorine inlets currently being used.

Table XII. Data on Four Consecutive Direct Chlorination Campaigns

Product	*Weight, pounds*	*Hf-Zr content pounds*	*Recovery Hf-Zr*	*Chlorine efficiency*
Input				
Oxide	7347	5877		
Chlorine	7592			
Output				
$HfCl_4$(raw)	10227	5696	96.9	59.8
Residues	315	142	2.4	
Losses		39	0.7	
	Total	5877	100.0	

Hours actual operation : 936
Product pounds per hr : 10.9
Residue pulled : 0.0313 pounds per pound of product (raw $HfCl_4$)
Chlorine duty : 0.742 pounds per pound of product (raw $HfCl_4$)
Power used : 0.757 kw hour per pound product (raw $HfCl_4$)

	Power input and temperature attained	
Chlorine preheater	0.25 kw	95°C
Charge area	5.50 kw	750°–1150°C
Cross-over pipe	0.50 kw	400°–500°C
Condenser — shell heater	2.00 kw	150°–250°C

The condenser is a cyclone type made of light-gauge nickel with a mild-steel jacket. The space between the jacket and the inner shell is baffled for circulating the pre-heated air used to maintain the proper condenser temperature. The waste gases pass to an after-condenser of the same design where the last traces of hafnium chloride are removed and then to the scrubbing towers of 4-inch diameter Pyrex glass. The first scrubbing tower is supplied with waste cooling water from the chlorinator, while the second, packed for 48 inches with 1-inch porcelain Raschig rings, functions with circulating 2*N* sodium hydroxide solution.

Since the first tower is unobstructed by packing, it is easy for an operator to observe the physical properties of waste gases and by close observation of the recorded temperatures on the chlorinator system power readings on the electrodes, and back pressure on the chlorine feed, he can obtain a uniform chlorination rate.

A trickle flow of CO_2 gas is fed into the gasket-sealed gas-tight feed hopper to prevent hafnium tetrachloride from entering and condensing in the plunger-type feeder.

An air vibrator is attached to the condenser at the top near the chloride inlet for use whenever the product needs to be shaken loose from the side

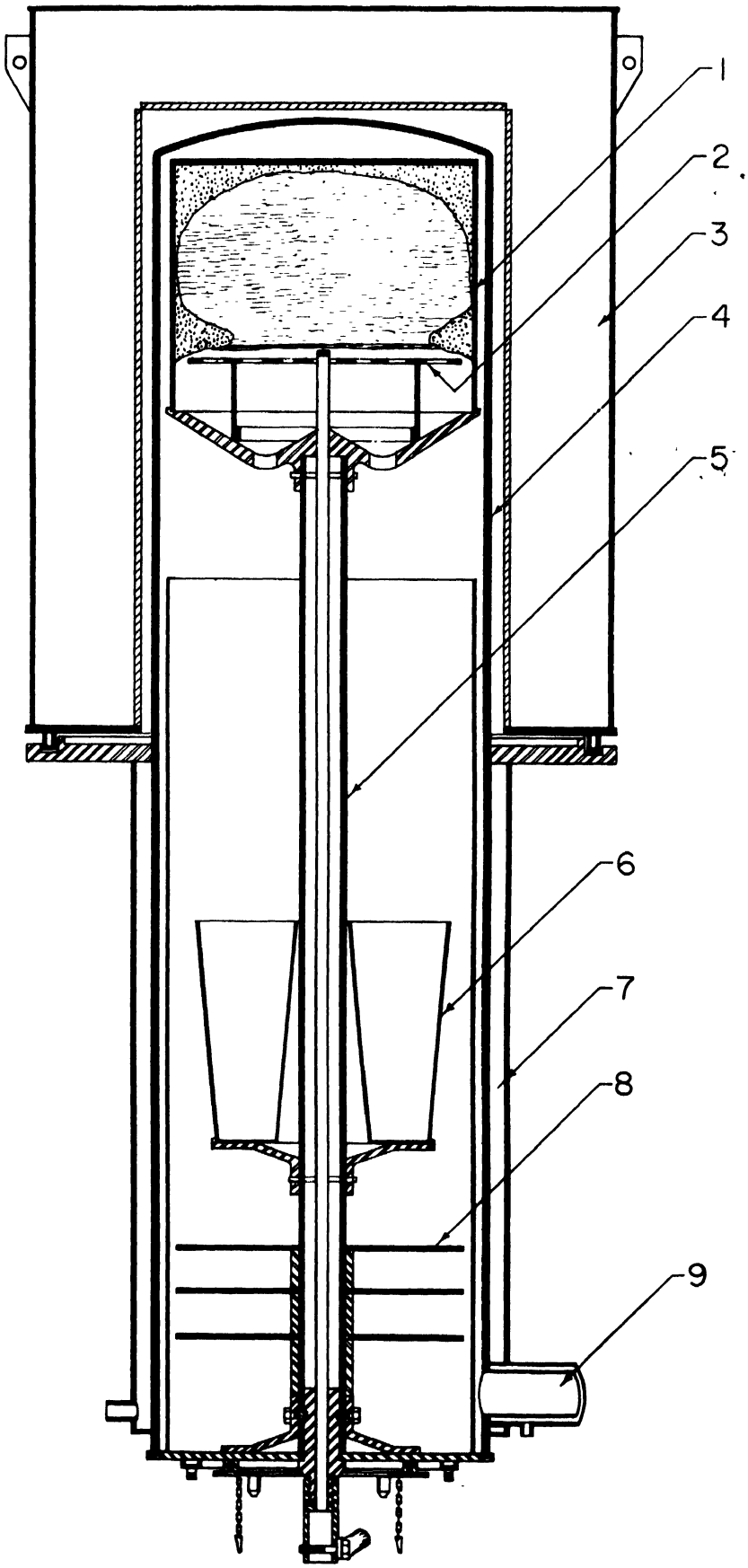


Figure 57. Distillation furnace

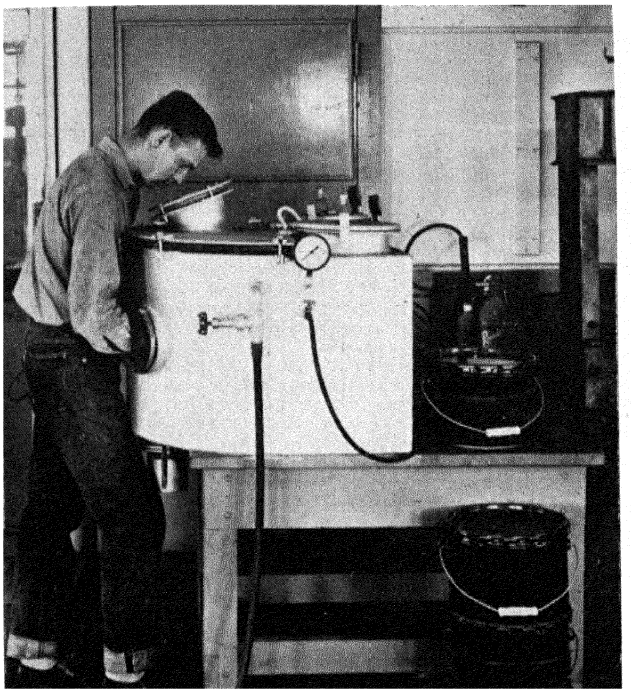


Figure 59. A helium atmosphere box for cleaning the sponge

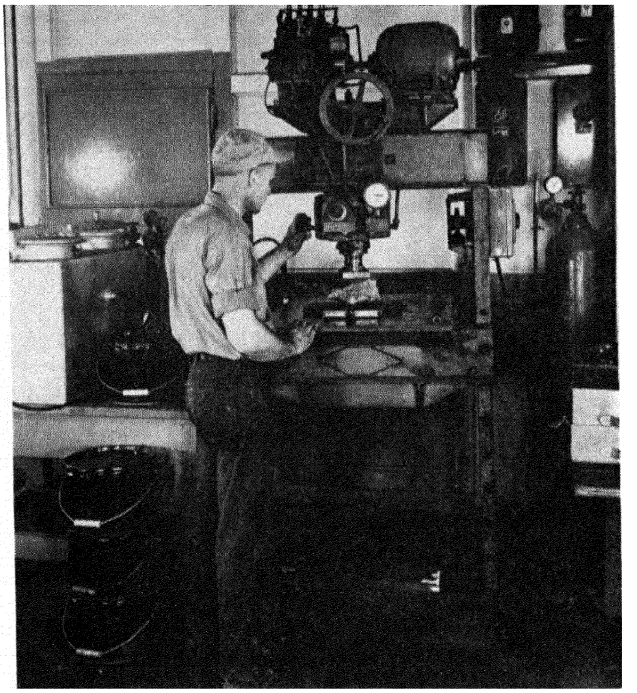


Figure 60. The sponge being crushed

walls to expose fresh condensing surface. This vibration has been found to also shake and loosen the bed of briquets so that little or no barring of an arched bed is found to be necessary.

The chlorination rate of 10 pounds of hafnium tetrachloride per hour carries enough heat through the necked-down shaft to keep the product from condensing in the entrance of the cross-over pipe and delivers the chloride to the condenser as shown in Fig. 51. The raw chloride produced is stored in sealed 55 gallon drums to await purification. Data from four chlorination runs are shown in Table XII.

Purification of the Raw Chloride

As described in a previous publication,[60] the raw chloride is purified by subliming in an inert atmosphere and simultaneously condensing on a water-cooled coil as shown in Figs. 52 and 53. Most of the objectionable impurities are eliminated in the residue. The raw chloride is charged (with baffles to promote heat transfer) into an Inconel can 25 inches in diameter and 40 inches high. This can and chloride then are lowered into the pit-type furnace containing 3 heating zones, the lower or subliming zone, the middle or condensing zone, and the lead-seal zone. A floating top is immediately set in the furnace and the lead-antimony seal is frozen. Paraffin added and frozen on top of the lead completes the seal and the furnace is evacuated to 25 mm of Hg with the lower zone set at 250°C. The furnace is back-filled with helium and after an hour of soaking at this temperature the evacuation is repeated This conditioning is to remove combined water and the more volatile chlorides such as the chlorides of titanium and silicon.

The lead seal is melted and the lower zone temperature gradually is raised while the expanding gases and volatile impurities are bled off. Air and then water cooling is applied to the coils to collect the purified dense chloride.

The temperature at which sublimation is carried out has been lowered and the purification time lengthened from that used in the purification of zirconium due to the possibility at a high temperature of carrying over oxychloride to the dense chloride. A temperature setting on the lower zone (subliming zone) of 575°C has been found adequate for maintaining the optimum rate. See data sheet in Table XIII, showing recoveries in each of the steps of the Kroll process.

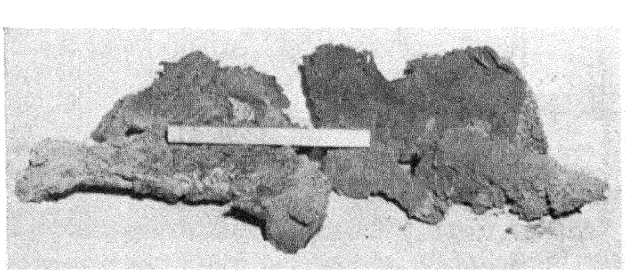


Figure 61. Hafnium sponge

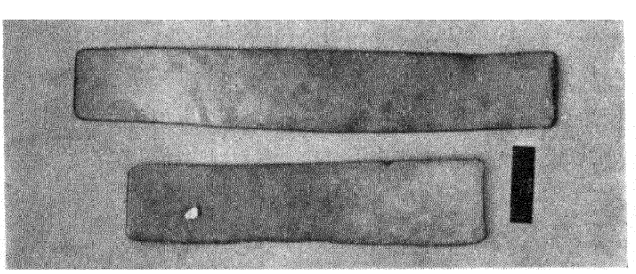


Figure 62. Hafnium sheet

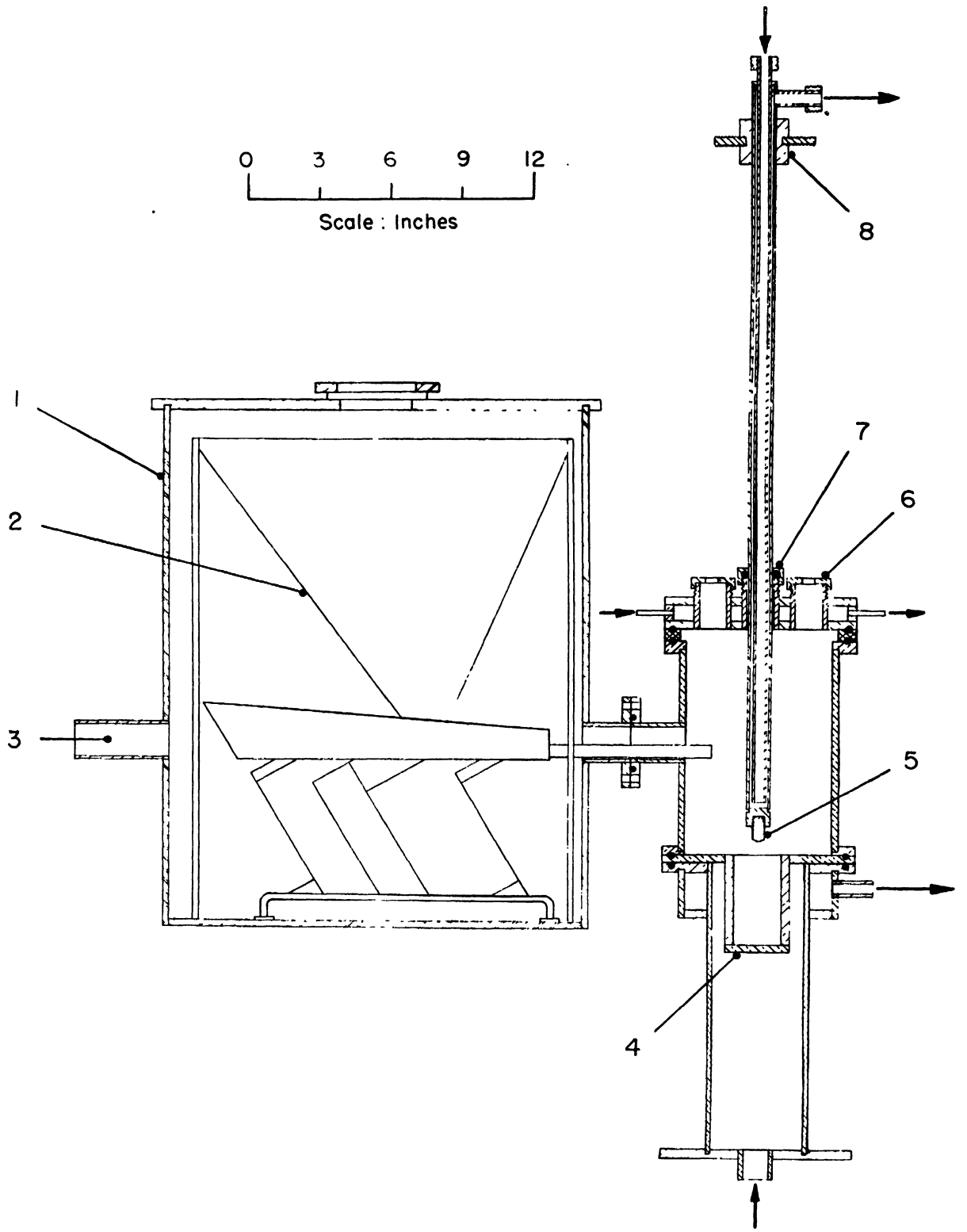


Figure 63. Nonconsumable-electric melting furnace

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Table XIII. Data Sheet on Recoveries for a Recent Run in the Reduction Plant

		Pounds	Per cent recovery
	Purification Step		
Input:	Raw $HfCl_4$	543	
Output:	Weight of dense ingot	509	93.7
	HfO_2 (oxide residue)	27	5.0 (recycled)
	Loss, handling	7	1.3
	Total		100.0
	Reduction Step		
Input:	$HfCl_4$ (dense ingot)	509	
	Magnesium (40% excess)	127	
Output:	Absorbed $HfCl_4$	496	97.4
	Vapor phase	4	0.8
	Loss, handling	9	1.8
	Total		100.0
	Distillation Step		
Input:	Net weight crucible contents	623	
Output:	Hafnium sponge	268	96.5 (of theoretical density)
	$MgCl_2$ and excess Mg	355	
	Over-all recovery		88.3

Reduction

The reduction of hafnium tetrachloride with magnesium is made in zirconium plant equipment without modification.

After the furnace has cooled sufficiently, the top with dense chloride on the coils is removed (Fig. 54) and placed in the reduction furnace which contains a stainless-steel crucible 25 inches in diameter and 20 inches high. This crucible contains 140 per cent of the theoretical magnesium required for reaction with the dense chloride and is covered with a baffle (as shown in Fig. 55) to exclude any oxide residue falling from the coils. The furnace is sealed as in the purification and evacuated to 3 mm of Hf with water cooling maintained on the coils, then back filled with helium. This is repeated, then the lead seal is melted, the lower zone set to 775°C, and the floating top to 450°C. Again the furnace is bled (Fig. 56) as the gases expand and the chloride begins to sublime. When the magnesium has melted, the $HfCl_4$ is sublimed by heating the middle zone and it reacts with the molten magnesium in the crucible. The sublimation rate is controlled by the middle-zone heating element and air on the coils. During the initial reaction, which lasts from 4 to 5 hours, the zone temperatures are controlled by additions of helium so that the furnace runs 50°C cooler than in a corresponding zirconium reduction, which is permitted to rise to 875°C. This has been found to give a cleaner reduction, and higher recovery of usable sponge. After the reduction is over (indicated by the necessity of adding helium to keep the top floating) the zone temperature at the reduction crucible is raised to 920°C and held for one hour. Any hafnium sponge which may be on the sidewalls of the crucible above the magnesium chloride cover appears to be cleaner if this high-finishing temperature is employed, and reduction byproducts are less pyrophoric when exposed to the atmosphere at the time of transfer to the salt removal furnace.

Vacuum Distillation

The equipment and operation are conventional for the Kroll process.[61]

In the reduction furnace the hafnium sponge is obtained as a magnesium saturated paste. In the distillation furnace (see Fig. 57) where the crucible is inverted, the sponge usually slumps and rests on the table. Some difficulty is experienced in removing the distilled sponge from the furnace because the sponge remains on the table rather than staying in the pot where it can be protected from burning by an inert atmosphere. Due to the pyrophoric nature of the material a self-locking table (see Fig. 58) was devised to take the place of the standard table. This is placed in the crucible and locked by two crossed rods when the crucible is transferred from the reduction to the distillation furnace. This self-locking table prevents movement of the sponge mass, keeping it confined within the crucible, and consequently prevents fires as the crucible is being handled after distillation.

Before the retort is opened the sponge is conditioned with air. This conditioning process begins at about 37°C (99°F) and is necessary to pacify the sponge surface so it will not ignite upon exposure

Table XIV. Analysis of Three Test Lots of Metal

Sample No.	$\frac{Zr}{Hf+Zr} \times 100$	O_2 ppm	Fe ppm	N	Cl	Al	Cu	Pb	Zn	Cr	Co
1.	1.4	650	400	10	150	30	100	30	<5	100	<10
2.	1.4	850	400	20	100	30	100	30	<5	100	<10
3.	1.3	950	400	30	200	50	50	20	50	<5	<10

Mn	Ni	Si	Ti	V	Mo	Cd	B	Sn
30	<5	100	<50	<20	<10	0.5	0.3	5
30	<5	100	<50	<20	<10	0.5	0.2	5
30	<5	20	<50	<20	<10	<0.05	0.2	<5

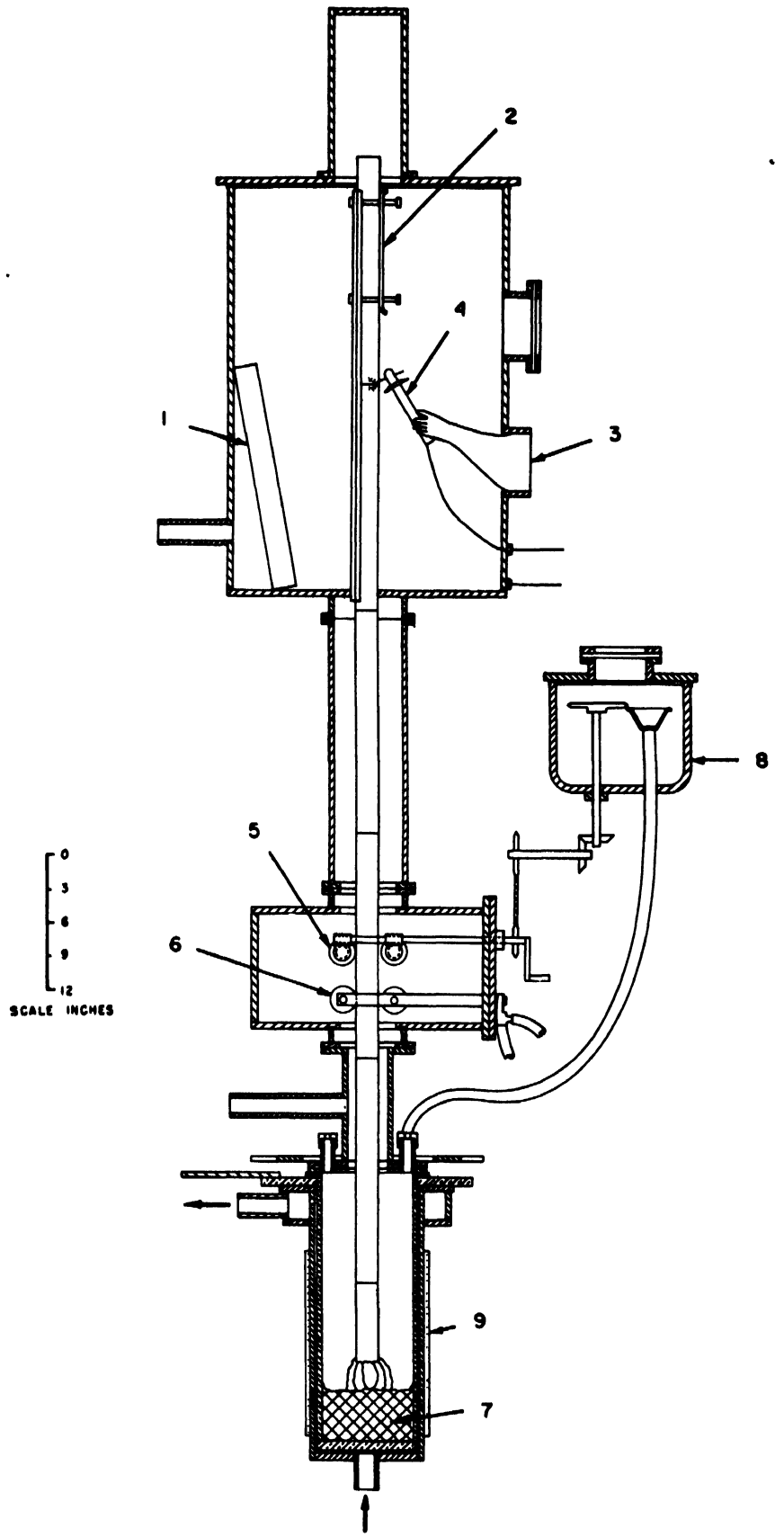

Figure 64. Consumable-electric melting furnace

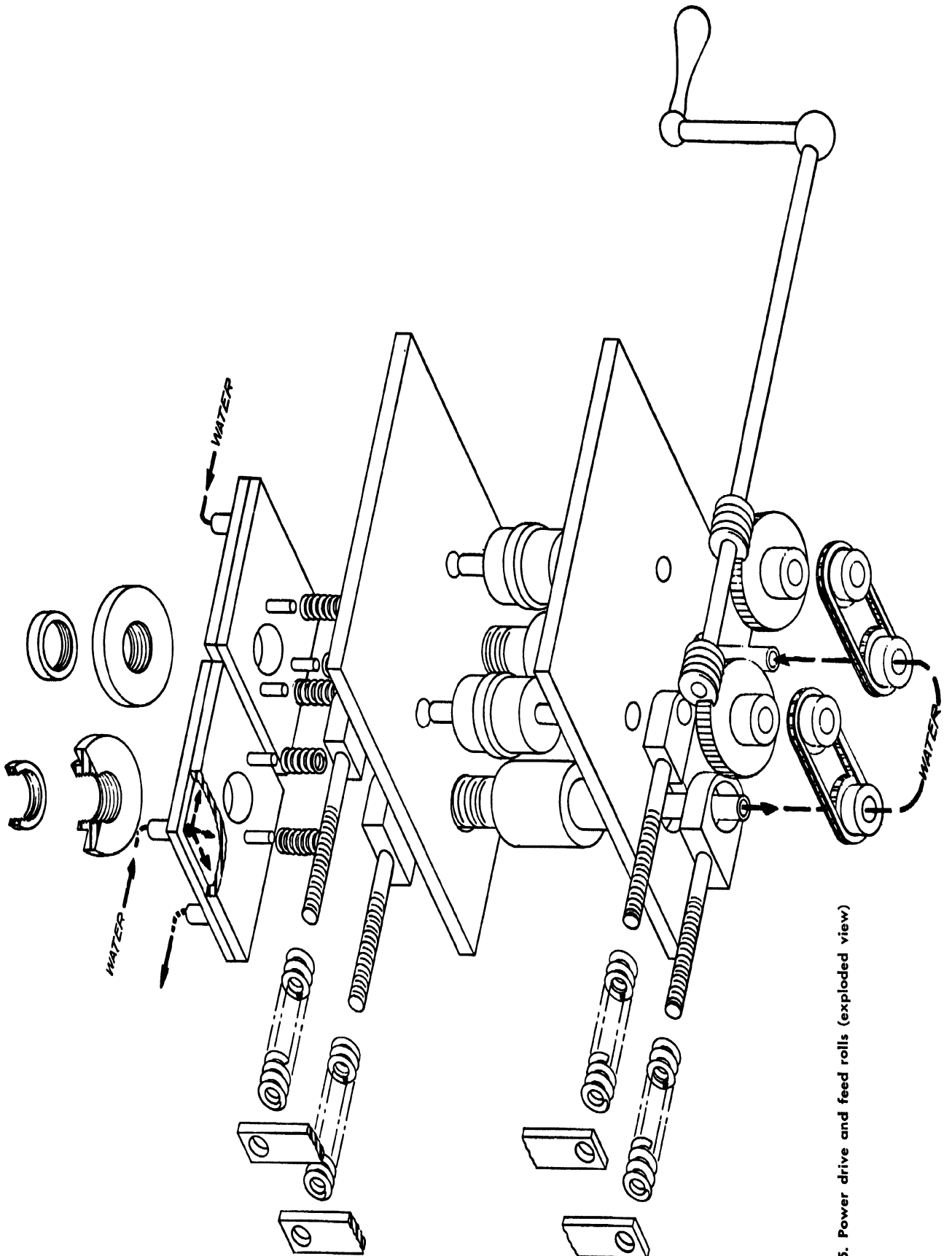

Figure 65. Power drive and feed rolls (exploded view)

to the normal atmosphere. To condition a charge, dry air is admitted slowly into the retort while the temperature is watched carefully. When atmospheric pressure is reached the air is immediately pumped out again. Room air then is admitted slowly and allowed to remain for one hour before being pumped out. The retort then is filled with helium and is ready to open. This conditioning period requires approximately 4 hours which is 1 hour longer than is required for zirconium.

Sponge Handling

A helium atmosphere box (Fig. 59) for cleaning the sponge is equipped with a power driven buffer. All sponge which had been in contact with the crucible or table is cleaned by wire brushing; and the sponge crushed and sized without the benefit of an inert atmosphere (see Fig. 60). The exercise of extreme care in all operations consistently produces a sponge similar in appearance and ease of handling to zirconium sponge. Very carefully controlled runs give a higher efficiency and the sponge shows crystal growth more nearly equal to zirconium.

Hafnium sponge (Fig. 61) is melted by consumable electrode arc methods and the ingots forged and rolled to sheet as shown in Fig. 62. All metal had a hardness of R_c 20 to 25 which is indicative of oxygen contamination. At such hardnesses the metal may not be considered cold ductile. The sponge can be purified by the iodide dissociation method to give metal having a reported hardness of R_b 78.

Analysis of three test lots of metal is listed in Table XIV.

All residues and metal scrap were burned in large porcelain dishes to hafnium oxide for recycling in the process.

MELTING

To the melter, zirconium presents three distinct difficulties: (1) it is extremely reactive in the molten state; (2) it getters all gases except the noble gases; and (3) sponge, upon heating, exhibits extreme spattering and boiling as the volatiles are released from the pores.

In the molten state zirconium approaches a universal solvent and the choice of a suitable refractory crucible is a difficult one. It is agreed generally that highly fired thoria is one of the most satisfactory crucible materials, although it too is slightly soluble in the molten metal. In addition, it is scarce and expensive. Highly-fired beryllia is fairly resistant to attack, but the hardening effect of small amounts of beryllium in zirconium eliminates its use. Dense grades of graphite may be used if small quantities of carbide can be tolerated.

Melting Methods

Two commercial techniques are available to melt zirconium, cold-crucible melting, and refractory-crucible melting. Cold-crucible melting is accomplished with electric-arc heating from either a zirconium consumable electrode, or a fixed electrode

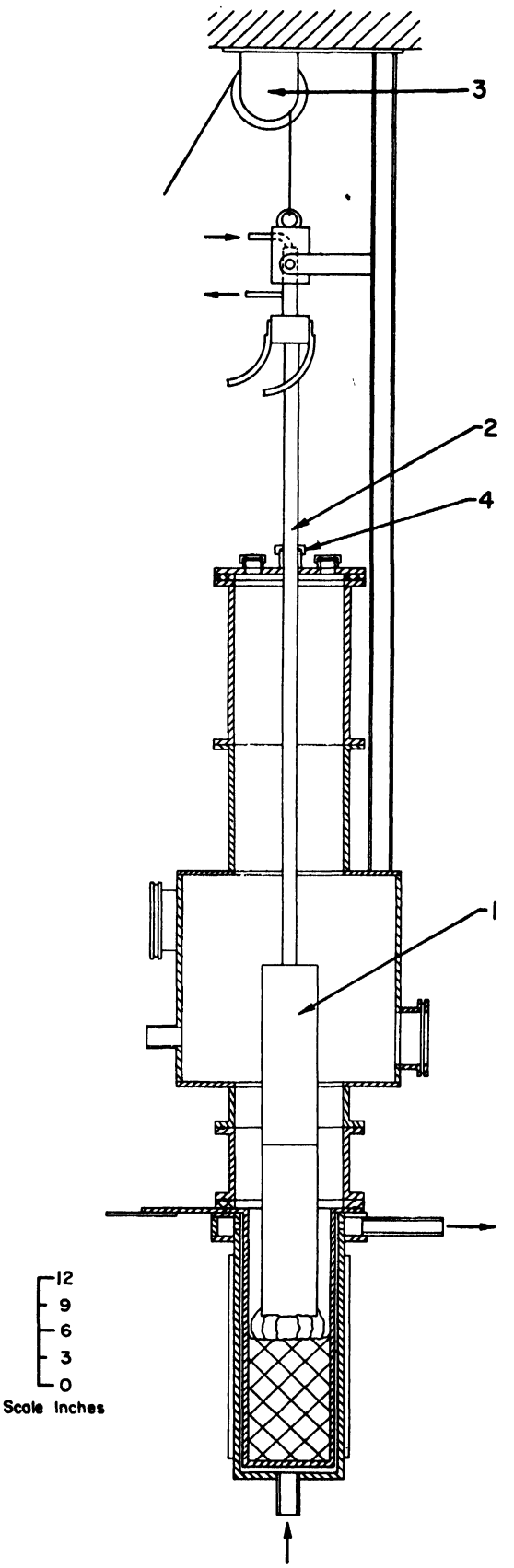

Figure 66. Remelt furnace

such as carbon or tungsten. Refractory crucibles may be heated by direct or indirect arc, electric induction, or resistance. The Bureau of Mines employs the consumable-electrode cold-crucible method for production melting because it eliminates the crucible and electrode as sources of contamination, and is adapted readily to inert atmosphere conditions. In addition, the non-consumable cold-crucible method and the resistance-heated graphite crucible techniques are used for small-scale work.

Non-Consumable Electrode Arc Melting

Kroll's original variation of von Bolton's furnace included the use of a tungsten non-consumable electrode and the original arc melting of zirconium was carried out at the Bureau of Mines in a similar furnace utilizing a water-cooled tungsten electrode.[63]

The furnace in present use is pictured in Fig. 63. As indicated, the essential parts include (1) a vacuum tank, (2) a vibrating feed hopper, (3) the vacuum line, (4) copper crucible, (5) the tungsten electrode, (6) eye piece, (7) O-ring gland, (8) negative power connection.

Directional control of the arc is effected by a large hand-manipulated alnico horseshoe magnet controlled by the furnace operator. A high frequency unit is placed in the electrode side of the dc circuit to assist in establishing the arc. The copper crucible is made from standard copper pipe with brazed-in collar-top and bottom. The arrangement permits the use of several sizes of cups to make melts varying in weight from 15-gram buttons to 25-pound ingots with no change of water jacket.

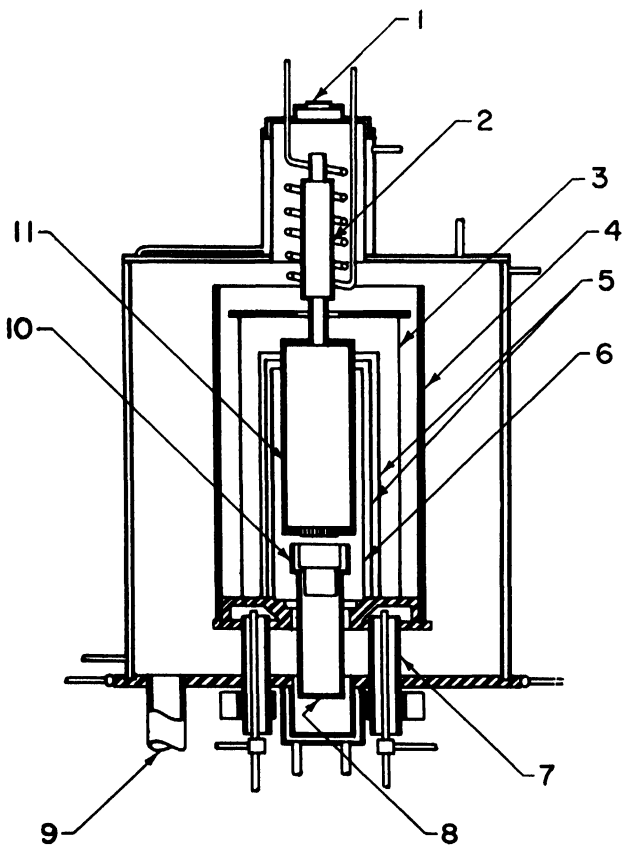

Figure 67. Graphite-resistor melting furnace: (1) eye piece; (2) condenser; (3) molybdenum shield; (4) quartz shield; (5) graphite shield; (6) resistor; (7) power leads; (8) mold; (9) vacuum line; (10) hot top; (11) crucible

Iodide process crystal bar may be melted without difficulty in this type furnace[63]. However, the melting of Kroll process sponge is not such a simple matter, since even small amounts of magnesium chloride causes the molten pool to boil and spatter. This spattering causes drops of zirconium to adhere to the electrode where they alloy with the tungsten, and finally fall into the melt. Actually only a small contamination results, and if the tungsten could be distributed evenly through the ingot no serious defects would result. This is not the case, however. The zirconium-tungsten alloy does not dissolve completely, but remains as distinct inhomogeneities, which cause hard spots when the ingots are reduced to sheets. Continued rolling often results in tears in the thin sheet.

In addition to the tungsten tips, thoriated tungsten, carbon, and tantalum have been used, with varying degrees of success. Rapid erosion and accompanying ingot contamination eliminates the use of carbon and tantalum. In practice thoriated tungsten tips are favored by the operators because lower arc temperatures result in lowered electrode consumption and contamination.

At the Bureau of Mines tungsten-arc melting has been used extensively in preparing small buttons for analysis and testing.

When a base plate containing several depressions is used, the method is especially adaptable to the preparation of alloys for phase diagram work. In this way several 50-gram buttons may be melted without opening the furnaces. Generally, the alloy is made by compacting sponge and alloying material, melting, turning the button, and remelting.

Consumable-Electrode Arc Melting

Despite the convenience and neatness of the tungsten or inert electrode type furnace, the possibility of electrode contamination eliminates its use as a practical production furnace, and modern-day efforts in melting development lean toward consumable-electrode arc melting.

The success of this technique depends to a large extent upon the availability of a sponge compacting device. The Bureau's efforts have been facilitated greatly by the use of a large triple-action powder-metallurgy press for the production of 2×2×20-inch compacts at a pressure of 50 tons per square inch.

Salient features of the furnace in use at present are shown schematically in Fig. 64: (1) a sponge compact, (2) a guide, (3) gloves, (4) welding electrode, (5) steel drive roll, (6) copper contactor roll, (7) ingot, (8) alloy feeder, (9) solenoid.

Continuous feeding is dependent on a method of joining the bars, since they are limited in length. This is accomplished by placing a stock of bars in a vacuum-tight tank mounted on top of the furnace

and welding them together as they are inserted into the feeding rolls. Welding is done with tungsten electrodes with an input of 25 volts and 100 amperes direct current. The electrical resistance of the joint section between two bars joined by inert-atmosphere tungsten-arc welding is less than that of an equivalent length of pressed bar.

A mechanical feeding device is provided to permit an easily advanced electrode feed. Essentially this mechanism consists of a set of steel feed rolls actuated by a manual or motor-driven source, and a pair of water-cooled copper rolls which act as electrical contacts for the power supply. An "exploded" sketch of the apparatus is shown in Fig. 65.

The melting crucible is fabricated from standard 4, 5, 6, 8, or 10-inch standard copper pipe with wall thicknesses of $\frac{3}{16}$ to $\frac{5}{16}$ inch. The water jacket around the coil is made from a non-magnetic material to permit the use of a solenoid consisting of a few thousand turns of No. 20 magnet wire wound directly on the water jacket. This provides a gentle stirring action to the pool of molten metal directly below the arc, and tends to center the arc. The quantity of cooling water varies with the diameter of the crucibles; the larger sizes often requiring as much as 120 gallons per minute.

Since the crucible serves as one electrode it must be insulated from the upper part of the furnace containing the power input rolling contacts. Power for melting is supplied by a series of 800 amp selenium welding rectifiers which operate from a 3-phase 440 volt line. This power supply provides a flexible source of energy for melting and can operate continuously at 60 per cent of the rated output.

Provision is made for continuous alloy additions during melting by metering to the melt powdered metal compacts or tablets from an auxiliary tank. For normal operation two men are required, a bar joiner who places the bars in the guides and welds the joints, and the melter, who controls the electrode feed in order to maintain an optimum melting rate.

Power input remains fairly constant for any size ingot. Satisfactory ingots may be made, by using the following power inputs:

Ingot diameter, inches		2	3	4	5
Power input, volts		25	28	30	40
Amperes		800	1000	1800	2500
Ingot diameter, inches	6	7	8	9	10
Power input, volts	40	40	40	40	40
Amperes	3500	4000	4500	5000	5500

The power input may be increased above this level in order to speed up the melting rate (a maximum of 40 volts, 4000 amps has been used without difficulty in the production of 5-inch ingots). A gradual cut-back in energy input prior to ending the melt prevents shrinking or "piping" in the ingot. The average power consumption for melting zirconium is about 0.25 kwh per pound.

For the production of homogeneous alloys double melting is practiced. Ingots produced in the furnace shown in Fig. 64 are faced on the ends, and drilled and tapped to receive a 1-inch stud screw. Several ingots then are joined end to end with zirconium connectors and remelted in reduced pressure atmosphere in equipment shown in Fig. 66. The parts numbered are described as follows: (1) first-melted ingots connected end to end, (2) water-cooled copper rod, (3) a winch, and (4) the O-ring gland. In operation the furnace is simple, having no moving parts except the electrode itself. Ten-inch diameter ingots weighing as much as 600 pounds are cast easily by this procedure.

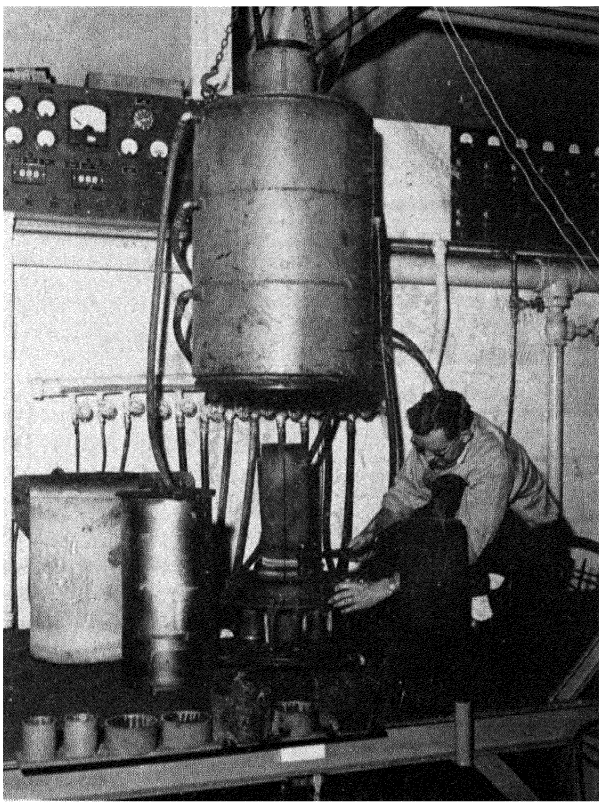

Figure 68. Graphite-resistor furnace, disassembled

The removal of the occluded hygroscopic salts from the sidewall of the first-melt ingots by scalping reduces contamination to a minimum. A nitrogen pick-up of 10 parts per million is considered higher than normal. Finished ingots generally contain about 0.1 per cent oxygen and 0.005 per cent nitrogen.

Consumable electrode ingots generally require scalping before hot working. Machining in a lathe removes the majority of sidewall and end imperfections. Some grinding may be necessary for local flaws.

The resulting ingots are inspected by ultrasonic reflectoscope and, wherever possible, all internal discontinuities are removed.

Resistor Furnace Melting

Melting furnaces heated by graphite resistors have been utilized for melting zirconium, and are valuable especially for melting skulls and odd-shaped pieces which cannot be made into consumable ingots.

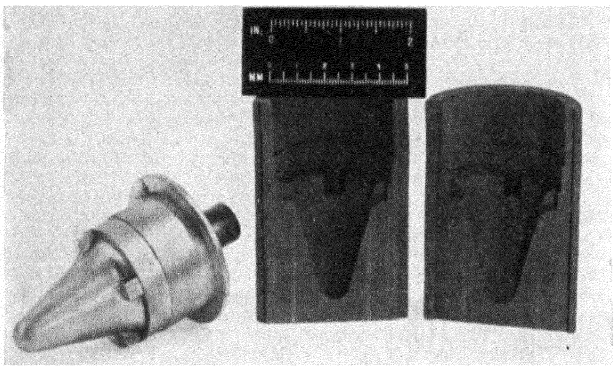

Figure 69. Graphite mold and zirconium casting

An economically operated single-phase, split-tube graphite-resistor-type batch furnace was used successfully for most of the early zirconium melting at Albany, Oregon.[64] Later an improved furnace which utilized two phase current and was capable of melting larger charges was developed.[65] It is essentially a resistance-heated graphite shell enclosed in a steel sleeve. The sketch (Fig. 67) gives the details of the assembly. Figure 68 is a photograph of the disassembled furnace, and shows the component parts.

The heating element is a graphite tube having equally spaced slots extending from the bottom to within one and one-half inches of the top. The lower or slotted end of the tube is connected mechanically and electrically to the four copper quadrants by means of solid copper wedges. Power is supplied by a two-phase-Scott-connected transformer of 75kw capacity, and fed through the base plate of the furnace by four water-cooled, vacuum-tight, insulated seals.

In production, all of the melting is done in a vacuum of about 20 to 100 microns. However, an inert gas atmosphere could be used, although the power consumption will be greater due to increased heat dissipation. When sponge was melted, the charge was compressed into briquets in order to increase the furnace capacity.

The crucible, by necessity, is made of graphite. Several grades have been tried, the most satisfactory being a dense A.U.C. grade material. Machined from solid stock, the crucible is about 5 inches in diameter and 10 inches high with ½-inch walls. Several pouring holes are drilled in the bottom and a small graphite cross is wedged just above the holes to reduce the vortex as the metal pours from the crucible.

In practice, the melting proceeds from the center, upward and downward, the bottom reaching the pouring temperature last due to the cooling effect of the bottom plate. When all of the charge has melted, the metal drains into the mold below. This mold is a tapered graphite cup with a removable bottom. A removable collar which acts as a funnel and hot-top surmounts the mold and is lost with each melt. The collar extends above the mold through a hole in the resistor and into the heated part of the furnace. It is effective in reducing ingot piping since the top of the casting remains liquid while the balance of the metal solidifies in the mold. The molten metal does not wet the cold mold, permitting its easy removal; however, the metal clings tenaciously to the hot top, and it has to be removed by machining.

Since the furnace operates in a vacuum, any volatiles contained in the sponge are eliminated. This material is collected in a water-cooled graphite tube which extends from the center of the crucible cover. In addition to zirconium, the somewhat pyrophoric dust contains manganese, calcium, magnesium, and magnesium chloride.

In addition to producing ingots, this type furnace is readily adaptable for casting accurate shapes. Graphite molds are required; otherwise no difficulties are encountered. A mold and casting are shown in Fig. 69.

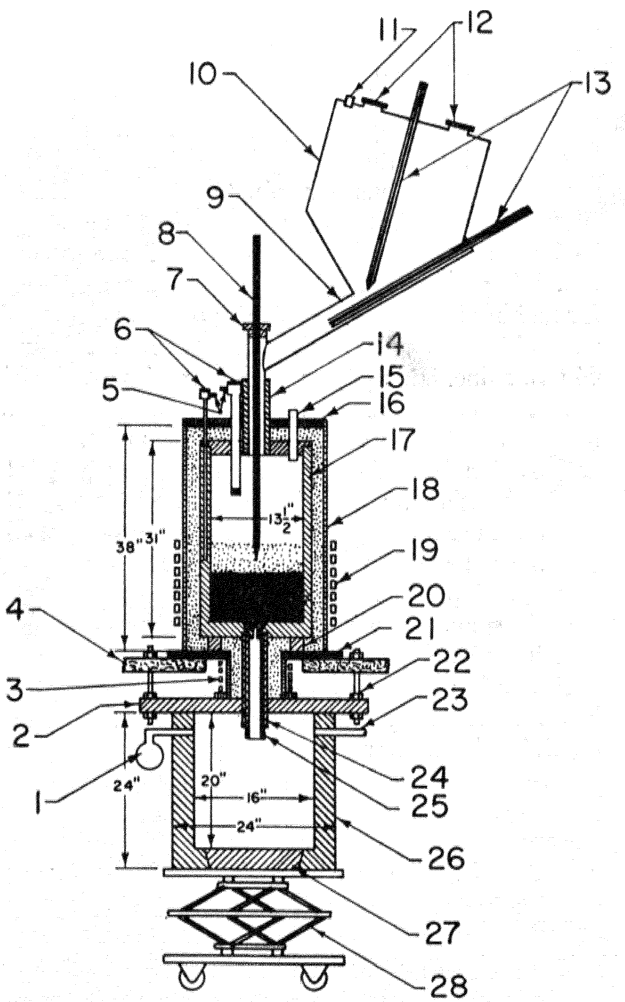

Figure 70. Induction melting furnace (Sutton, Gee, and DeLong): (1) balloon; (2) 3 in. × 30 in. dia graphite plate; (3) water-cooled copper coil; (4) aluminum support; (5) argon inlet; (6) sight glass; (7) graphite bushing; (8) poke rod; (9) sheet steel feed connection; (10) hopper; (11) argon inlet; (12) sight glass; (13) feed poke rods; (14) graphite feed tube; (15) argon vent tube; (16) ½ in. transite; (17) graphite melting pot; (18) 18 in. dia silica shell; (19) water cooled copper coil; (20) porous carbon blocks; (21) 1 in. transite; (22) ½ in. dia hangers; (23) argon inlet; (24) threaded graphite sleeve; (25) removable raphite sleeve; (26) graphite mold; (27) graphite plug; (28) jack

The furnace described has a capacity of sixteen 20-pound ingots per 24-hour day. A typical operating schedule is:

	Minutes
Unload and recharge	5
Rough vacuum pump	5
Main vacuum pumps	25
Heat and pour	25
Cool	30
Total	90

The only major source of contamination is from the crucible. Unlike titanium, which dissolves as much as two per cent carbon, the maximum content of zirconium is always much lower. The usual carbon pick-up amounts to 0.15 to 0.25 per cent. In a test ingot remelted six times, the carbon did not exceed 0.35 per cent. The resulting carbide appears as randomly distributed stringers within the grains. Under normal working methods the stringers are broken and scattered and do not affect materially the mechanical properties of the metals. Except for some nuclear uses which demand high corrosion resistance the presence of this small amount may be acceptable.

Induction Furnace Melting

Induction melting of zirconium, although possible, is not likely to be adopted commercially for several reasons: (1) it is essentially a batch process, limited in size by the melting crucible; (2) carbon crucibles must be used, with the inevitable addition of carbon; and (3) the limited life of the graphite casting mold unnecessarily increases the cost of the metal. Sutton, Gee, and DeLong[66] have described an induction furnace for melting titanium which would be suitable for zirconium. It is shown in Fig. 70. In operation, the outlet crucible is plugged with a piece of metal and the crucible and hopper are filled with sponge; the entire system is flushed with helium or argon. The crucible is heated and as the charge melts additional sponge is fed from the hopper. When the desired amount of metal has been melted, the tapping coil is energized and the molten metal drains into the graphite mold.

A swirling action resulting from the induced field continually washes the walls of the melting crucible and encourages carbon pick-up. This contamination is held to a minimum by melting the charge as rapidly as possible without allowing the charge to become super-heated, and pouring as soon as a suitable casting temperature is reached.

Bureau of Mines work has been confined to small scale experiment. Only a limited amount of work has been done, however; most attention being directed to more attractive methods.

Present day experience with high-capacity continuous arc-melting furnaces appears to have surpassed the induction-melting techniques, and it is not likely that the method will find extended use as a means of melting zirconium sponge or scrap.

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Process for Separation of Zirconium and Hafnium

By J. Hure,* and R. Saint-James,† France

A number of processes for zirconium-hafnium separation have been mentioned in the literature (precipitation, crystallization, fractional distillations, extraction of various compounds).

Of all these processes, countercurrent extraction by a solvent seems to us the one most easily usable on an industrial scale.

We know that tributyl phosphate extracts a number of metallic compounds: uranyl, thorium, and cerium nitrates and various thiocyanates. It therefore seems reasonable to study the possibilities of tributyl phosphate in this field. As it happens, other separations with this solvent have been studied in various laboratories of the Commissariat à l'Energie Atomique.

Tributyl phosphate is a rather viscous solvent, whose density is near that of water. It must be diluted in order to make decantation easier. Dearomatized white spirit was finally chosen as the diluent: this is a liquid with a low specific gravity (0.74); chemically inert to nitric acid, at least in the cold; insoluble in water; and of low toxicity. It should, however, be mentioned that its flash point is 26°C. For safety reasons, we chose a fraction with a relatively low vapor tension (distillate between 140 and 190°C).

I. STUDY OF SEPARATION CONDITIONS

Preliminary tests showed that a nitrate medium seemed most favorable to extraction; but many other factors enter into the separation process. We studied, in succession, the influence of the acidity, that of the NO_3^- concentration, the role of the cation accompanying the NO_3^- ion, and finally the influence of the zirconium concentration of the solution.

The main conclusions of this study may be simply summarized:[1] Nitric acid favored both the extraction of the zirconium and that of hafnium (Figs. 1 and 2). Sodium nitrate favors zirconium more than hafnium. At equal concentration, ammonium nitrate is a less effective salting-out agent than sodium nitrate. However, if its concentration in the solution is increased, the increase of α_{Zr} is accompanied by a decrease in the ratio $\beta = \alpha_{Zr}/\alpha_{Hf}$. Calcium nitrate has the drawback of yielding rather viscous solutions, which are undesirable when liquid-liquid countercurrent flow is contemplated. Furthermore, it decreases even more the low solubility of zirconium in a nitrate medium.

The greatest number of experiments, however, dealt with the role of the zirconium-salt concentration of the solution. As a general rule, the extraction of zirconium decreases as the concentration increases. Nevertheless, the values obtained vary with the history of the solution: depending on whether the solutions were diluted by renewed extractions or by the addition of a $NaNO_3$-HNO_3 mixture with a composition similar to that of the initial solution.

It is a noteworthy fact that the extraction of hafnium follows that of zirconium, and that beyond a concentration of 5 gm of zirconium per liter, the coefficient of separation β is virtually invariable (Figs. 3 and 4). This remark applies at least to solutions containing zirconium and hafnium in the ratio $Hf/Zr \simeq 2\%$. Finally, when a 45 gm/l aqueous solution of zirconium is shaken with a mixture of tributyl phosphate and white spirit (60% tributyl), we find after decantation the appearance of a third phase, apparently of the white spirit. This phenomenon has been pointed out in the case of thorium. It seems that the phenomenon appears at much lower concentrations for zirconium.

II. WASHING THE SOLUTION

The zirconium extracted by the solvent still contains 0.1% of hafnium approximately. Rewashing this solvent with the $NaNO_3$-HNO_3 mixture used by us up to the present time, might logically be expected to produce re-extraction by the aqueous phase of a portion of the zirconium and hafnium contained in the solvent, the extraction coefficients α_{Zr} and α_{Hf} keeping the same values as in the preceeding operation. This leads to a further purification of the zirconium.

III. RECOVERY OF PURIFIED ZIRCONIUM

The recovery can be performed by washing with water or using a solution of some electrolyte. It is also conceivable to use a complex-forming agent such as a fluoride, but this raises questions of equipment, in addition to being rather expensive, and, furthermore, would prevent further precipitation of the zirconium.

Original language: French.

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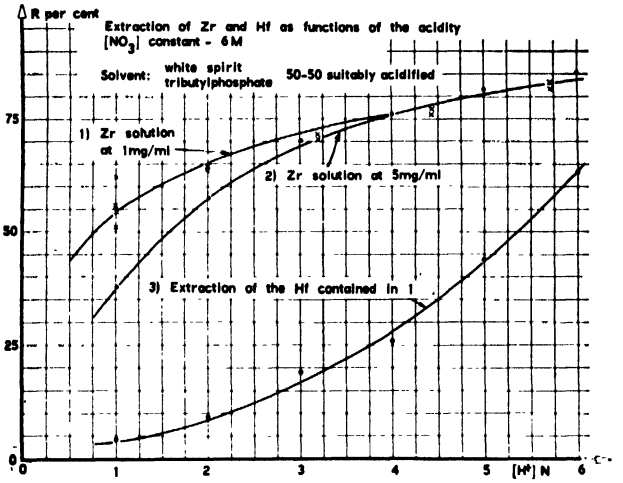
R per cent
Extraction of Zr and Hf as functions of the acidity
[NO3] constant - 6 M
Solvent: white spirit tributylphosphate 50-50 suitably acidified
1) Zr solution at 1mg/ml
2) Zr solution at 5mg/ml
3) Extraction of the Hf contained in 1
[H+] N

Figure 1. Extraction of Zr and Hf as functions of the acidity

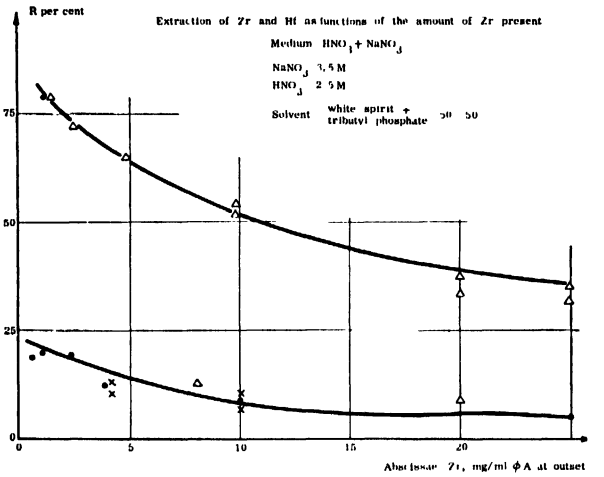
R per cent
Extraction of Zr and Hf as functions of the amount of Zr present
Medium HNO3 + NaNO3
NaNO3 3.5 M
HNO3 2.5 M
Solvent white spirit + tributyl phosphate 50 50

Figure 3. Extraction of Zr and Hf as functions of the amount of Zr present

At all events, the recovery problem is rather delicate. In point of fact, the zirconium seems to go through a process of evolution in the nitrate solvent, although the reasons for this aging and its details have not yet been determined. The net effect is to prevent complete recovery of the zirconium contained in the solvent. At the present time, water washing must be performed directly upon leaving the mixer-settler.

IV. SOLVENT RECYCLE

It appears to be possible to perform at least ten cycles with the solvent, simply washed in water and reacidified. At the present time, the loss of tributyl phosphate by dissolution in the water or partial hydrolysis is of the order of 2%. However, the difficulties encountered are of a different nature: as the recycles mount up, the emulsion requires more and more time to break up.

V. PILOT PLANT (SEE "FLOW SHEET", FIG. 5)

On the pilot level, we now work under the following conditions:

Zirconium solution containing 30 grams of zirconium per liter, 3 moles of nitric acid per liter, and 3.5 moles of sodium nitrate per liter.

Solvent containing 60% of tributyl phosphate, 40% of white spirit (by volume), and 1.6 mole of nitric acid per liter, also water in the amount carried along on acidification, equal to about 3%.

Washing solution containing 3 moles of nitric acid per liter and 3.5 moles of sodium nitrate per liter.

Although the extraction coefficient α_{Zr} varies with the zirconium concentration, some approximate evaluation can be made by supposing α constant and equal to 1.5; it is likewise assumed that the ratio of the rates of flow of the solvent and the aqueous phase $V/V' = 1$ in the extraction process. If x_1 is the zirconium concentration in the residual aqueous phase, and x_{n+1} the zirconium concentration at the intake of the apparatus, which is supposed to be equivalent to n theoretical trays, then by a well-known calculation, we find that:

$$\frac{x_1}{x_{n+1}} = \frac{[(V/V')\alpha] - 1}{[(V/V')\alpha]^n - 1}$$

If we take a yield of 90%, with V equal to V', it is possible to calculate the number of theoretical trays required for satisfactory operation:

$$\frac{1}{9} = \frac{1.5 - 1}{(1.5)^n - 1} \rightarrow (1.5)^n = 5.5$$

$$n = \frac{\log 5.5}{\log 1.5} = 4$$

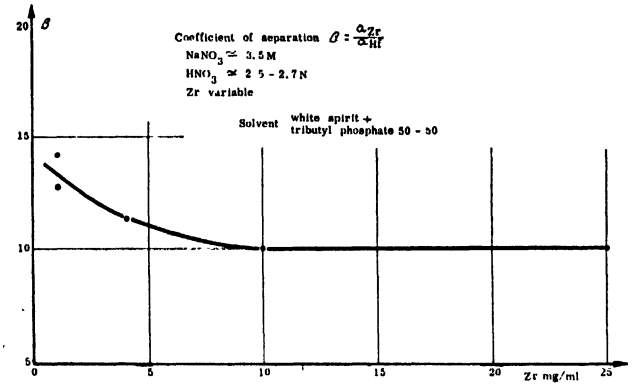
β
Coefficient of separation β = αZr/αHf
NaNO3 ≃ 3.5 M
HNO3 ≃ 2.5 - 2.7 N
Zr variable
Solvent white spirit + tributyl phosphate 50 - 50
Zr mg/ml

Figure 2

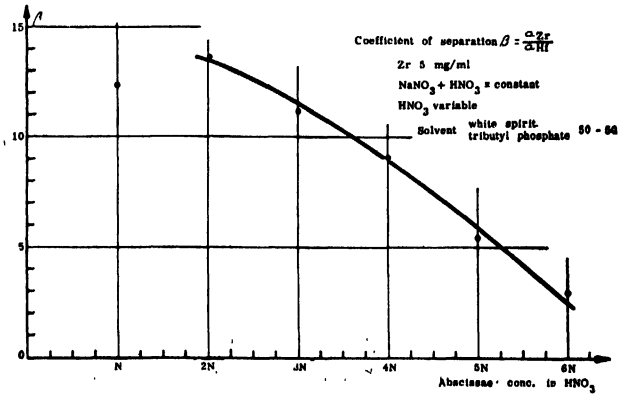
β
Coefficient of separation β = αZr/αHf
Zr 5 mg/ml
NaNO3 + HNO3 = constant
HNO3 variable
Solvent white spirit tributyl phosphate 50 - 50
Abscissae: conc. in HNO3

Figure 4

Since we also know that the zirconium extracted in this way contains about 0.1% of hafnium, and that the degree of purity desired is 0.01% of hafnium, and taking α_{Hf} to be constant and in the neighborhood of 0.11, with the rate of flow equal to 0.5 in the washing operation, it is possible in the same way to calculate the number of theoretical trays required. We find: $1 < n < 2$.

We would therefore need six theoretical trays to conduct the entire purification process with a 90% zirconium yield.

The apparatus employed is a mixer-settler comprising nine elements, each having a capacity of 15 liters and an efficiency of about 0.75 theoretical trays.

Mixture of the phases is effected in each mixer by a centrifugal pump, which at the same time circulates the emulsion. The decanted phases run into the next mixing compartment by an overflow system. Since the total output is 200 liters/hour, the average tray in each thickener is $(15/200) \times 60 =$ 4½ minutes.

Six elements are devoted to extraction and three to washing.

Under the conditions mentioned above, and with the apparatus employed at the present time, it is possible to produce 1 kg of zirconium per hour, containing less than 0.02% of hafnium. The residual aqueous phases then contain a mixture of zirconium and hafnium along with various impurities. The concentration of this mixture varies between 20 and 40% hafnium.

We give, as an example, the operating curve and the equilibrium curve obtained during an operation with the mixer-settler (Fig. 6):

22 gm/l zirconium solution containing 2.4% hafnium.

Solvent containing 60% tributyl phosphate.

Rates of flow: solvent, 100 liters/hour; zirconium, 48 liters/hour; wash, 48 liters/hour.

Concentration of zirconium-enriched solvent: 10 gm Zr/liter.

Hafnium concentration of residual aqueous phases $Hf/(Hf + Zr) = 42\%$.

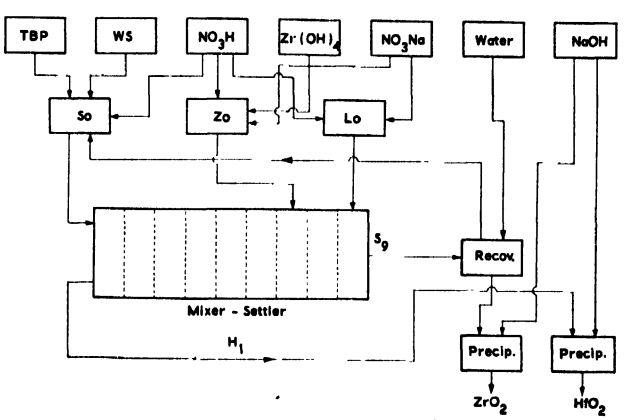

Figure 5. Flow-sheet

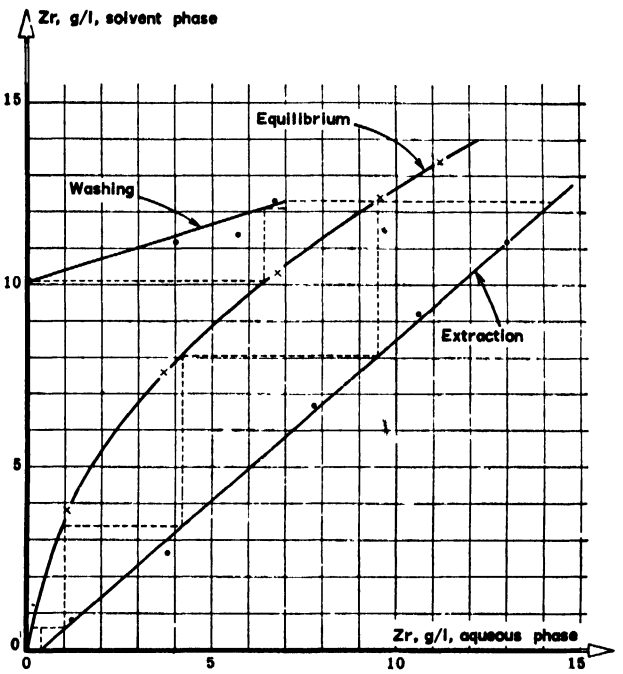

Figure 6. Operating and equilibrium curves obtained in an operation with mixer-settler

Purity of zirconium obtained $Hf/Zr < 3 \cdot 10^{-4}$.

ANALYTICAL METHODS

The zirconium is determined either by colorimetry for small amounts,[2] or by volumetric analysis, using the complex ion.[3]

The first hafnium determinations were made by the Nuclear Physics Service of the Commissariat à l'Energie Atomique, which used a method of deferred coincidences to measure the period of the metastable state of the irradiated hafnium. This measurement was very sensitive and was not interfered with by any foreign element.

The determinations are now regularly made by spectrography of the precipitated zirconium for specimens with low hafnium content, and on the solutions for the concentrated bottoms.

Finally, certain samples, particularly low in hafnium are determined by irradiation at regular periods, using the 19-second period for hafnium.

ACKNOWLEDGEMENT

We take this occasion to express our gratitude to MM. Artaud, Ballini, and Leveque for their collaboration.

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Separation of Hafnium from Zirconium by Vapour Phase Dechlorination

By Brahm Prakash and C. V. Sundaram,* India

The zircon sands of India contain about 3 per cent hafnium expressed as Hf × 100/Hf + Zr. As a consequence of the very close similarity between the chemical behaviour of zirconium and hafnium, the problem of their separation is attended with unusual difficulties, although several methods have been proposed for this purpose from time to time. The recognition of the importance of hafnium-free zirconium as a structural and cladding material for reactor applications has accentuated interest in this problem during recent years.

Among the methods of separation which have shown promise, mention may be made of fractional crystallisation, fractional precipitation, fractional sublimation, solvent extraction, and adsorption methods such as ion-exchange and chromatography. De Boer and van Arkel[1] obtained zirconium-enriched crystals by fractional crystallisation of the diammonium hexafluoro salts of hafnium and zirconium, and Hevesy and Madsden[2] extended the procedure to obtain zirconium-free hafnium compounds. Based on the relative instability of the hafnium coordination complexes, Prandtl[3] suggested and Schumb and Pittman[4] developed a procedure for effecting the separation by fractional precipitation of the ferrocyanides from aqueous solutions containing oxalate and sulphate ions. Larsen, Ferneleus and Quill[5] found that fractional precipitation of the phosphates from strongly acid solutions resulted in progressive enrichment in hafnium in the first precipitates. Fractional sublimation of the addition compounds of the tetrachlorides of zirconium and hafnium with phosphorus oxychloride was the means adopted by Gruen and Katz[6] to effect a separation. More recently, solvent extraction, ion exchange and other adsorption methods have come into prominence for this application. Thus Fischer and collaborators[7], in studying the distribution of the thiocyanate complexes of zirconium and hafnium between ether and water, have found that the zirconium complex gets preferentially extracted by ether. Huffman and Beaufait[8] investigated the distribution of thenoyltrifluoro acetone complexes, and Schultz and Larsen[9] of the trifluoroacetyl acetone complexes between benzene and water, and both investigations have shown that organic phase. For ion-exchange separation, both the zirconium complexes preferentially enter the anionic and cationic exchange resins have been investigated. Thus Kraus and Moore[10], and Huffman and Lilly[11] have separated hafnium from zirconium by fractional elution of the zirconium adsorbed on the anion exchange resins Dowex-1 and Amberlite (IR-400). Cation-exchange resins have been used by Street and Seaborg[12] and later by Newnham[13] for selective elution of the impregnated hafnium. Lister[14] has determined the conditions required for selective elution of zirconium instead of hafnium. Hansen and co-workers[15] have observed that activated silica gel preferentially adsorbs hafnium from a methanol solution of the chlorides. Another attempt at adsorption separation by paper-strip chromatography has been described by Kember and Wells.[16]

Among the methods reviewed, fractional crystallisation, fractional precipitation and sublimation have the disadvantage of requiring laborious multiple-step treatments. Adsorption separation on silica gel would require solvents of high purity. Solvent extraction and ion exchange seem applicable, in principle, to continuous flow operation and are therefore quite promising.

In India, investigations on the separation of hafnium from zirconium, have been directed towards examining the feasibility of (*a*) ion exchange, and (*b*) vapour-phase dechlorination, as means of separation. The process and the main conclusions of the investigation on the ion-exchange process[17] which was undertaken at the National Chemical Laboratories of India, are summarised below:

"Zircon from the Travancore sands was converted into potassium fluoro-zirconate and the fluoro complexes of zirconium and hafnium equilibriated with the anion-exchange resin Amberlite-IR-400, either in the chloride or sulphate form. Thereafter, the impregnated resin was eluted with 1.0*N* sulphuric acid at a flow rate of 0.3 to 0.4 cm^3 per minute when hafnium got preferentially leached. Under optimum conditions, a maximum of 90 per cent hafnium-free zirconium was recovered."

The investigation reported here deals with attempts to devise a separation process based on the selective decomposition of zirconium tetrachloride to its oxide which would leave hafnium as a readily volatile chloride.

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THEORETICAL CONSIDERATIONS

The conversion of the tetrachlorides of zirconium and hafnium to their respective oxides by reaction with oxygen may be represented by the following equations:

$$ZrCl_4\ (g) + O_2 \rightleftharpoons ZrO_2 + 2\,Cl_2 \qquad (1)$$

$$HfCl_4\ (g) + O_2 \rightleftharpoons HfO_2 + 2\,Cl_2 \qquad (2)$$

The standard free energy change for the two reactions, as a function of temperature, has been calculated from thermodynamic data available in literature.[18,19] These calculations lead to the following relationships:

$$(\Delta F^\circ)_{Zr} = -58{,}525 - 8.956T \log T - 1.041 \times 10^{-3}\,T^2 + 1.3915 \times 10^5\,T^{-1} + 50.75T$$

and,

$$(\Delta F^\circ)_{Hf} = +21{,}642 - 10.68T \log T - 1.181 \times 10^{-3}\,T^2 + 1.4515 \times 10^5\,T^{-1} + 58.86T$$

From the above expression, the free energy change, equilibrium constant (K_P), and equilibrium P_{Cl_2} : P_{O_2} ratios were calculated for different temperatures, and the data for the two reactions are presented in Table I.

These calculations show that the conversion of zirconium tetrachloride to the oxide is highly feasible whereas the conversion of hafnium tetrachloride is not. Thus at 1200°C, as will be observed from Table I, the equilibrium $P_{Cl_2} : P_{O_2}$ ratio for oxide formation is 114 for the zirconium reaction and it equals 6.97×10^{-5} for the hafnium reaction. The spread of the equilibrium ratios is even greater at lower temperatures. If, therefore, the chlorides in the vapour state are reacted with a gas mixture composed of chlorine and oxygen, in a ratio intermediate between the values for the two reactions, zirconium chloride should form the oxide and the more stable hafnium chloride should distil over unchanged. Alternately, the mixed oxides could be chlorinated under the above conditions when hafnium oxide would be expected to form the volatile chloride, leaving zirconium oxide behind. For accomplishing such a fractionation, it is necessary that the two oxides should have the same thermodynamic properties in the mixture as they have individually. This is not a justifiable assumption in this case because the two oxides probably form solid solutions. For this reason and because direct gas-solid chlorination of the refractory oxides would require a high temperature, vapour phase dechlorination was preferred. Though chlorination of the mixed oxides could be carried out in the presence of carbon, thermodynamic calculations show that under these conditions, selectivity of separation is greatly reduced.

EXPERIMENTAL METHODS AND RESULTS

The process for the separation of hafnium from zirconium in the zircon sands consisted of the following steps: (*a*) production of anhydrous zirconium chloride from zircon; (*b*) purification of the chloride to free it from contaminants other than hafnium; (*c*) vapour phase dechlorination for hafnium removal.

Production of Zirconium Chloride

The anhydrous chloride may be prepared by chlorination of zircon-carbon[20] or zirconia-carbon briquettes or by chlorination of zirconium carbide. Direct chlorination of zircon-carbon compacts, however, requires high temperatures of the order of 1000°C and the presence of silica in the zircon leads to excessive consumption of chlorine. The chlorination of zirconia-carbon compacts, though readily achieved, would require the preparation of zirconium oxide from the mineral zircon by relatively costly procedures. In this investigation, therefore, the chloride was prepared via the carbide.

A direct arc furnace was fabricated for the reduction of zircon to the carbide. The charge which consisted of zircon and charcoal in the proportion of 4:1 by weight was fed continuously into the furnace through a screw-conveyor at the top. During arcing, voluminous fumes of silicon monoxide (which oxidised in air) were produced and the carbide was obtained as a residue in the form of dense, bluish-grey blocks having a metallic lustre. The furnace made about one pound of carbide per hour.

Table I. Thermodynamic Data on the Dechlorination of the Chlorides of Zirconium and Hafnium

Temp. °C	Calories $(\Delta F^\circ)_{Zr}$	Calories $(\Delta F^\circ)_{Hf}$	$(K_p)_{Zr}$	$(K_p)_{Hf}$	$\left(\frac{P_{Cl_2}}{P_{O_2}}\right)_{Zr}$	$\left(\frac{P_{Cl_2}}{P_{O_2}}\right)_{Hf}$
500	−39,740	+42,780	1.70×10^{11}	8.13×10^{-13}	4.12×10^5	9.02×10^{-7}
600	−37,850	+44,880	2.99×10^9	5.75×10^{-12}	5.46×10^4	2.40×10^{-6}
700	−36,080	+46,880	1.24×10^8	2.95×10^{-11}	1.11×10^4	5.43×10^{-6}
800	−34,260	+48,850	9.48×10^6	1.13×10^{-10}	3.08×10^3	1.06×10^{-5}
900	−32,550	+50,730	1.16×10^6	3.53×10^{-10}	1.08×10^3	1.88×10^{-5}
1000	−30,900	+52,540	2.02×10^5	9.55×10^{-10}	4.50×10^2	3.09×10^{-5}
1100	−29,300	+54,310	4.60×10^4	2.27×10^{-9}	2.15×10^2	4.76×10^{-5}
1200	−27,740	+56,040	1.30×10^4	4.85×10^{-9}	1.14×10^2	6.97×10^{-5}

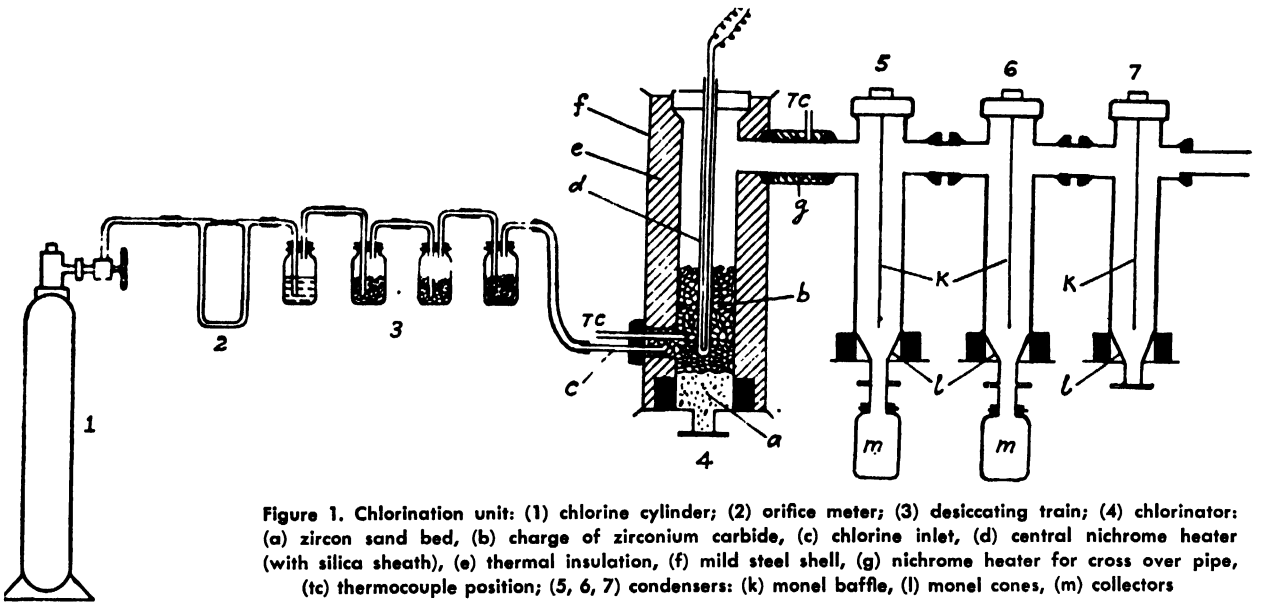

Figure 1. Chlorination unit: (1) chlorine cylinder; (2) orifice meter; (3) desiccating train; (4) chlorinator: (a) zircon sand bed, (b) charge of zirconium carbide, (c) chlorine inlet, (d) central nichrome heater (with silica sheath), (e) thermal insulation, (f) mild steel shell, (g) nichrome heater for cross over pipe, (tc) thermocouple position; (5, 6, 7) condensers: (k) monel baffle, (l) monel cones, (m) collectors

Chlorination of the Carbide

A special chlorinator unit was designed for conversion of the carbide into zirconium chloride and is shown in Fig. 1. The unit consisted of a vertical shaft furnace (4) made from an acid- and heat-resistant stoneware pipe (height: 36 inches, inside diameter: 6 inches, and wall thickness: 0.75 inches). The furnace communicated with a system of three stoneware condenser pipes (5,6,7) (height: 24 inches, and inside diameter: 6 inches), arranged in sequence. The furnace was heated from the centre by means of a nichrome heating element, sheathed in a one-inch diameter silica tube (*d*) closed at the bottom. The inlet pipe from the furnace shaft to the condenser was electrically heated with nichrome in order to prevent clogging of the passage. The furnace and the cross-over pipes were enclosed in a mild steel shell and the space between the shell and the stoneware pipes was packed with asbestos lagging. The condenser pipes were provided with monel baffles (*k*) to facilitate condensation of the chloride, and monel cones (*l*) were fitted at their bottom to direct the condensed chloride into glass- collectors situated below. The whole unit was supported in a mild steel frame.

In order to start the operation, the shaft furnace was charged from the top with zircon sand to form a bottom-bed, and thereafter zirconium carbide, crushed to a size of ¼ to ⅛ inch, was charged into the furnace to a height of about 12 inches. The furnace was sealed at the top and chlorine gas introduced at the rate of one pound per hour from a chlorine cylinder, via a flow-meter and a desiccating train. After flushing the furnace and the condensers free of air, heat was switched on. Chlorination was observed to commence at about 500°C as indicated by a sudden rise in the furnace temperature due to exothermicity of the chlorination reaction. The chloride collected in the glass-collectors below the monel cones and was in the form of a yellowish-white, fluffy powder. The powder is very hygroscopic and therefore presents problems in collection and storage. The unit gave an output of about 1.5 pounds of zirconium chloride per hour. Analysis of a typical sample (expressed in terms of oxides) showed 0.10 per cent silicon, 0.06 per cent titanium, and 0.18 per cent iron.

Purification of Zirconium Tetrachloride

As the subsequent selective dechlorination gave zirconium oxide as the end-product, it was considered desirable to free the chloride of its associated impurities such as silicon, titanium and iron at this stage. On account of their low volatilization points, the chlorides of titanium and silicon (b. pts. 136°C and 57°C respectively) would be separable by fractional distillation, but the separation of iron would require prior reduction of ferric chloride (sb. pt.: 319°C) to the relatively non-volatile ferrous chloride. A batch-purification unit, as shown in Fig. 2, was therefore set up for this purpose. The crude zirconium chloride was charged into the Pyrex distillation flask (1) which was radiation-heated by nichrome elements carried on the asbestos insulation of oven (4). The condenser bulb (3) was maintained at 200°C by simmerstat control, so that the silicon and titanium chlorides might escape as volatiles. The elbow-ground-glass joint (2) was kept at 450°C to avoid condensation of the chloride in this region during distillation. The entire assembly was flushed with hydrogen and the crude chloride soaked for one hour at 250°C in the reducing atmosphere of hydrogen. The temperature was gradually raised to 500°C when the purified chlorides of zirconium and hafnium condensed as white and compact crystalline powder in the condenser (3). After one fractionation, the sublimate was found to be free from silicon and gave an average analysis of 0.011 per cent iron and 0.0024 per cent titanium. The chlorides initially

contained 0.10 per cent silicon, 0.06 per cent titanium and 0.18 per cent iron.

Selective Dechlorination

The purified chloride, obtained in the previous step, contained 2.54 per cent HfO_2 in terms of the hafnia plus zirconia content of the product. For effecting the separation by reacting the gaseous chloride with oxygen and chlorine under controlled $P_{Cl_2} : P_{O_2}$ ratios at selected temperatures, a number of experimental set-ups was devised. The results obtained demonstrated the feasibility of fractionation into (1) a zirconium oxide residue relatively low in hafnium, and (2) a volatile chloride which was high in hafnium. A design for one such apparatus is shown in Fig. 3. The hafnium-containing chloride was kept inside a silica tube-furnace (S) which was wound with nichrome and controlled by a simmerstat. The chloride was volatilised at a relatively low temperature of the order of 300–325°C in a current of dry chlorine and the vapour led into a vertical tube-furnace (V) where it reacted with a down-coming stream of chlorine and oxygen at selected temperatures. For conducting dechlorination at higher temperatures, silica was substituted for Pyrex glass in the vertical reaction-chamber. Zirconium oxide, formed as a result of reaction with oxygen, deposited as a white powder in the collector, (M) and formed one fraction, whereas the unreacted chloride was caught in the condensers (C). The condensate was subsequently leached with dilute hydrochloric acid, filtered, and the hydroxides precipitated from it ig-

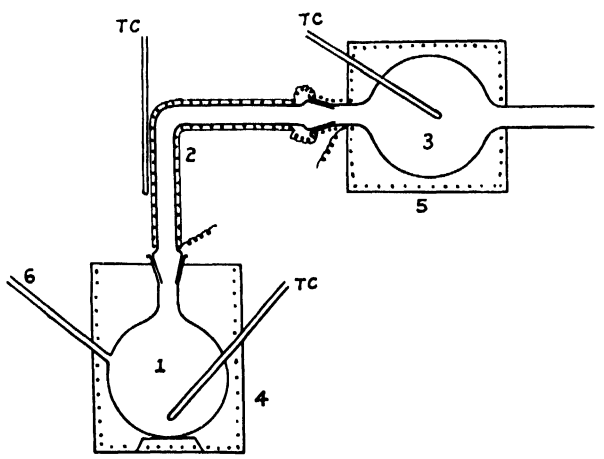

Figure 2. Distillation set-up for the purification of zirconium tetrachloride: (1) distillation flask; (2) elbow ground glass joint (heated with nichrome); (3) condenser flask; (4, 5) box type ovens; (6) inlet for pure, dry H_2; (s.c.) thermocouple position

nited to oxide to give the second fraction. Both the fractions were analysed spectrographically for their hafnium-contents. It was thus found that with a chlorine to oxygen ratio of 1:2 and a furnace temperature of 800°C, the residue contained 1.4 per cent hafnia after reaction for one hour, and the volatiles contained ≈ 25 per cent hafnia; with a chlorine to oxygen ratio of 1:1, the temperature at 500°C and reaction-time as two hours, the hafnia content of zirconia was 1.29 per cent while the volatiles contained above 25 per cent hafnia. The recovery of zirconia was 90 to 97 per cent. Similar results on hafnium-separation were obtained over a wide range of $P_{Cl_2} : P_{O_2}$ ratios and temperatures.

It will thus be observed that under optimum conditions, a single treatment results in lowering the hafnium content of the oxide by about 50 per cent. Further tests have been conducted in which bri-

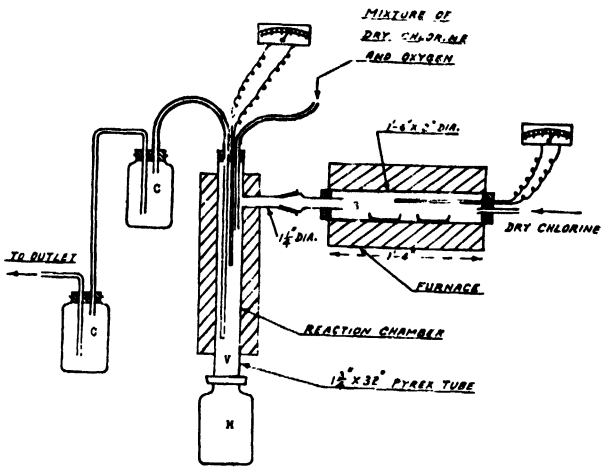

Figure 3. Vapour-phase dechlorination

quetted zirconia-charcoal or zirconium carbide has been chlorinated in one step, and the resulting chloride directly led into the reaction-furnace for treatment with oxygen and chlorine under controlled conditions. The results of such tests have again confirmed the separation of the chloride into a low and a high hafnium-containing fraction. Further work is in progress.

ACKNOWLEDGEMENT

The authors would like to thank Dr. J. Shankar, Chemist, Department of Atomic Energy, for conducting spectrographic analyses of numerous samples.

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Separation of Hafnium from Zirconium and Production of Pure Zirconium Dioxide

By N. P. Sajin and E. A. Pepelyaeva, USSR

When zirconium is used in the atomic energy reactors it is essential to purify it from the associated hafnium admixture, because hafnium possesses a great neutron capture cross section.

Of late the research workers have been paying great attention to the question of obtaining metallic zirconium and high purity initial materials free from hafnium and other elements.

The separation of hafnium from zirconium is one of the complicated problems of chemistry, inasmuch as the affinity of these elements make it difficult to separate them by one operation.*

Until recently the problem of separation of hafnium from zirconium was not considered essential from the practical point of view and the investigations were carried out chiefly for the purpose of scientific research, since for the usual application of zirconium and its compounds in various fields of technique the presence of hafnium in zirconium as a permanent admixture has not been detrimental.

At present the problem of separation of hafnium from zirconium is attracting an ever increasing interest of the scientists. The preparations of zirconium containing from 1 to 2% of hafnium are not considered as "chemically pure," since a zirconium containing only a thousandth per cent of hafnium is required.

It is possible to make the following classification of the numerous methods of zirconium and hafnium separation: (1) method of fractional crystallization of zirconium and hafnium salts;[1,2] (2) method of fractional precipitation;[3] (3) method of selective extraction;[4] (4) method of chromotographic adsorption and ionic exchange;[5,6,7] (5) method of fractional distillation.[8]

Many of the above described methods of hafnium and zirconium separation have been tried out by research workers of the Soviet Union (Poluektov and others) and in a number of cases good results as to the obtaining of zirconium free from hafnium and hafnium with a minimum content of zirconium were obtained (Vinarov and others).

This report describes the method of separation of hafnium from zirconium by fractional crystallization of bifluorides of zirconium (hafnium) and potassium. This method was developed by Sajin and others.

The method of fractional crystallization of zirconium and hafnium was investigated earlier.[1,2] A rather simple method of decomposition of the zirconium mineral (a compound of zircon and baddeleyite), worked out in 1950 by Soviet researchers Vaks and Pepelyaeva, served as a basis for the application of this method of zirconium and hafnium separation.[9]

Decomposition of zircon and baddeleyite by this method is accomplished by sintering of this mineral with potassium silicofluoride and potassium chloride with subsequent obtaining of potassium fluozirconate as a final product. The combination of the fluosilicate method of zircon decomposition and the fractional crystallization permits carrying out the separation of hafnium from zirconium by simple technological process, utilizing inexpensive materials.

PRODUCING OF POTASSIUM FLUOZIRCONATE FROM ZIRCONIC CONCENTRATE

Zirconic concentrate ground to 200 mesh (containing app. 60% ZrO_2) is mixed with potassium silico-fluoride and potassium chloride (the application of potassium chloride promotes the most complete decomposition of zircon).

The obtained charge is sintered in a rotary furnace (Fig. 1) at a temperature of 650–700°C.

The given temperature is an optimum one which is confirmed by the analysis of interdependency curve of zircon decomposition and sintering temperature as shown in Fig. 2.

The zirconium content in sinter is 13.0–14% of Zr, that is, equivalent to 40.0–43.0% of K_2ZrF_6. In order to transform the obtained potassium fluozirconate into solution, the crushed sinter is leached by a weak solution of hydrochloric acid (1% HCl by volume) and flushing water, left from the washing of an insoluble residue of the previous charge.

The leaching is accomplished by heating to a temperature of 85°C and stirring within 1.5–2.0 hours, at a ratio $S:L = 1:7$.

After leaching, the solution is left to precipitate.

The clarified solution of potassium fluo-zirconate is poured into an apparatus for crystallization and the precipitate is washed with water heated to the

Original language: Russian.

* The similarity of chemical properties of hafnium and zirconium is explained by the similarity of their atomic radii:

$r_{Zr} = 1.59$Å $\qquad r_{Hf} = 1.60$Å

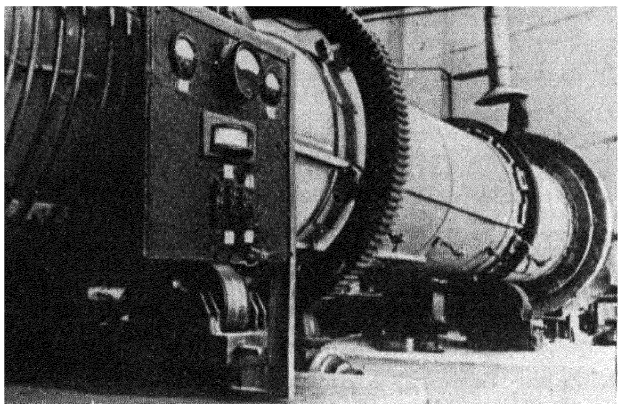

Figure 1. Rotary furnace for zircon decomposition

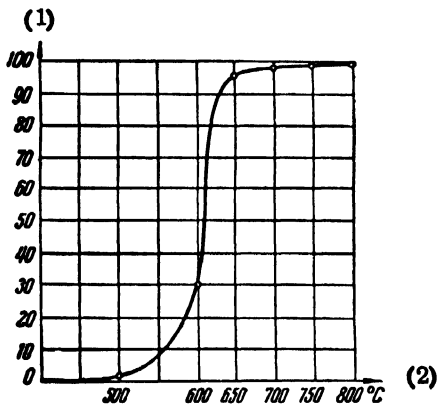

Figure 2. Dependence of zircon decomposition on the temperature of sintering. (1) Decomposition per cent (2) Temperature. During sintering of zircon with potassium silico-fluoride the decomposition of zircon is accompanied by a formation of the fluozirconate of potassium and the silicon dioxide according to the scheme:

$$ZrO_2 \cdot SiO_2 + 2KF \cdot SiF_4 \rightarrow K_2ZrF_6 + 2SiO_2$$

The decomposition of zircon in this reaction is 97.0—98.9%. The obtained sinter represents rounded off and slightly fused granules with an average size 0.5—10 mm (Figs. 3 and 4). The sinter is crushed to 100 mesh

temperature of 80°C. The clarified water is used for leaching of a new portion of sinter.

The solution of potassium fluo-zirconate is cooled and the following crystallization takes place:

$$K_2ZrF_6 \ (+ \ 1.5\text{–}2.5\% \ K_2HfF_6)$$

The crystals formed at this process are squeezed out and washed with water.

The chemical composition of potassium fluo-zirconate obtained from zirconic concentrates of the Azov shore deposits is as follows: Zr+Hf, 31.89–32.00%; K, 27.2–27.6%; F, 39.9–40.05%; Fe, 0.044–0.045%; Ti, 0.041–0.042%; Si, 0.06–0.07%; Cl, 0.006–0.008%; Hf, 1.5–2.5% (relative to Zr).

SEPARATION OF HAFNIUM FROM ZIRCONIUM BY FRACTIONAL CRYSTALLIZATION OF POTASSIUM FLUOZIRCONATE

Potassium fluozirconate obtained from zirconic concentrates contains up to 2.5% of hafnium (relative to zirconium).

The separation of hafnium from zirconium was accomplished by a method of fractional crystallization based on the different solubility of K_2ZrF_6 and K_2HfF_6. The solubility of potassium fluohafniate salts is higher than that of fluo-zirconate and therefore the accumulation of hafnium in the mother solution and the decrease of it in the potassium fluozirconate takes place at the fractional crystallization.

At present time, a number of methods have been developed, permitting, through several operations, to achieve a complete separation of zirconium from hafnium. However, the successful solution of the problem of obtaining potassium fluozirconate from zirconic concentrates and the simplicity of conducting the fractional crystallization process requiring no additional reagents (besides distilled water), permitted to utilize this method for producing zirconium free from hafnium.

This report presents some data on the research of the separation of hafnium from zirconium and establishing the required conditions necessary for fractional crystallization of potassium fluozirconate.

While conducting the fractional crystallization process, the potassium fluozirconate was dissolved in distilled water at a certain temperature of the solution and fixed concentration of K_2ZrF_6; thereupon the solution was cooled off to permit the separation

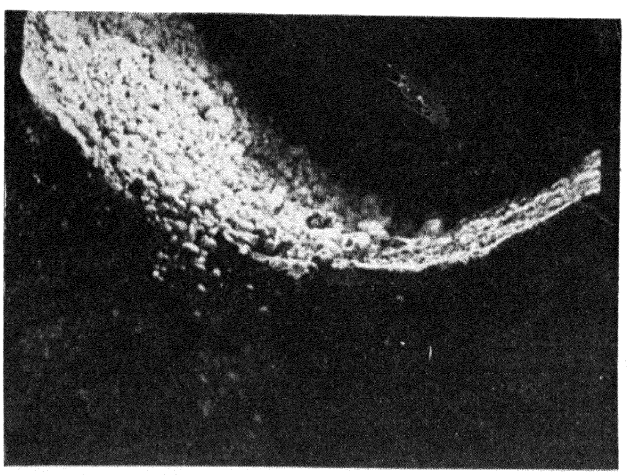

Figure 3. Sinter coming out from rotary furnace

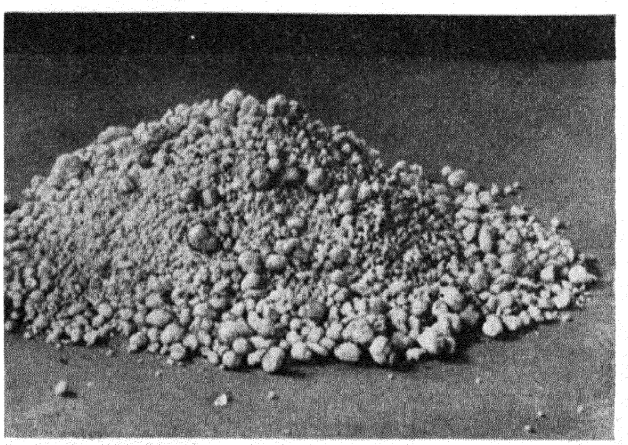

Figure 4. Uncrushed sinter

of crystals from the solution, which were then again subjected to recrystallization (solubility of K_2ZrF_6 at 100°C is 250 gm per liter and at 19°C correspondingly 16.3 gm per liter).

Conditions and number of crystallizations were determined, which secured both the maximum separation of hafnium and the yield of pure potassium fluozirconate.

The investigations have resulted in a quite satisfactory separation of hafnium: after 16–18 crystallizations the potassium fluozirconate was obtained containing a few thousandths per cent of hafnium.

The yield of purified potassium fluozirconate at the crystallization in aqueous solutions, i.e., after using water for dissolution at each crystallization, is not high and after 16 crystallizations the yield is about 10% from the initial content.

By utilizing the mother solutions left after crystallization from the previous run it was possible to attain a greater yield, about 80% without changing the degree of hafnium separation during this process.

The fractional crystallization with application of the mother solution from the previous run was carried out in the following way: the mother solution from the recrystallization of the previous run was poured into an apparatus made of stainless steel (which is used both for dissolving of potassium fluozirconate and for its crystallization) and potassium fluozirconate was added in ratio: $S:L = 1:7$ (0.5 mol of K_2ZrF_6 per liter). Dissolution is accomplished by heating to a temperature up to 80–90°C, then the solution is cooled and crystals of the potassium fluozirconate are formed.

After finishing crystallization the used mother solution is poured out into a receptacle, the mother solution left from the previous run is poured over the crystals and the next crystallization is performed.

A necessary number of crystallizations is carried out likewise, with distilled water used during the two last separation processes. The first and the second mother solutions, greatly concentrated by hafnium are taken out of the crystallization cycle and are evaporated to ⅕–⅙ of their volume.

The isolated crystals are returned for crystallization by adding them to the initial potassium fluozirconate at the first crystallization of a new run of zirconic concentrates; zirconium hydroxide containing about 6% of hafnium (in relation to zirconium) is precipitated from the solution by reaction with ammonia (NH_3). This hydroxide is used for obtaining concentrate and hafnium dioxide by ionic exchange or by the extraction with solvents. The hafnium content in fluozirconate after 16–18 crystallizations is less than 0.01% (in relation to zirconium). The determination of hafnium was effected with the help of a spectral-arc method, its sensitivity is 0.003%. The experimental results of hafnium separation from zirconium by fractional crystallization of potassium fluozirconate are shown in Fig. 5.

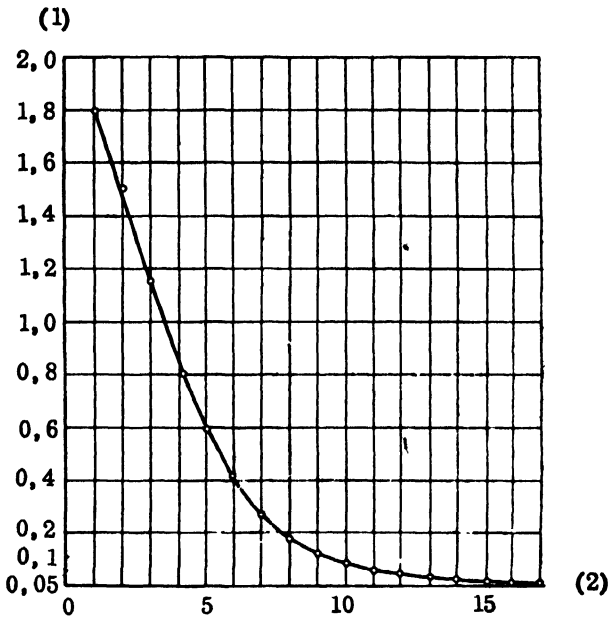

Figure 5. Separation of hafnium from zirconium by fractional crystallization of potassium fluozirconate; (1) hafnium content in % (in relation to zirconium); (2) crystallization

The chemical composition of potassium fluozirconate freed from hafnium by fractional crystallization is shown below (in %): Zr, 32.08–32.21; K, 26.89–27.24; F, 40.0–40.2; Fe, 0.02–0.03; Ti, 0.014–0.017; Si, 0.033–0.036; Hf, < 0.01 (in relation to Zr).

The yield of potassium fluozirconate free from hafnium is about 80%.

OBTAINING ZIRCONIUM DIOXIDE FREE FROM HAFNIUM

As a rule, zirconium dioxide is obtained from hydroxide of zirconium by calcination. A solution of 25 per cent of ammonia (NH_3) was used for the precipitation of zirconium hydroxide from liquid potassium fluozirconate.

The potassium fluozirconate was dissolved in distilled water at a temperature of 50° to 60°C (25–30 gm of K_2ZrF_6 per liter†) and in ammonia taken in excess of 150 per cent against the theoretically required. Zirconium hydroxide was precipitated by pouring the solution of potassium fluozirconate into ammonia. After precipitation and settling, the mother solution was poured off in a receptacle while hydroxide was washed off with distilled water from fluosalts, with a periodic addition (from 2 to 3 times) of ammonia in an amount of ~0.5 per cent of NH_3. The washed off hydroxide of zirconium was subjected to squeezing, drying and calcinating at a temperature of 900°C converting it to zirconium dioxide.

While conducting the investigations on the precipitation of zirconium hydroxide from potassium fluozirconate, the following peculiarities were ob-

† When precipitation is carried out from a solution of higher concentration of K_2ZrF_6, the washing of fluosalts is quite difficult.

served. Firstly, a necessity to pour a solution of potassium fluozirconate into ammonia during the precipitation process was established, in order to carry out the precipitation all the time with an excess of the precipitating factor. During this process of precipitation of ammonia to the solution of potassium fluozirconate leads to the formation of zirconium hydroxide–$Zr(OH)_4$–simultaneously with hydrate of zirconyl–$ZrO(OH)_2$–in the form of fine-dispersed precipitate and also in the colloid form. In the course of this process full precipitation of zirconium is not achieved and the washing of the hydroxide precipitate is rather difficult.

Another peculiarity is the behaviour of iron and titanium admixtures. It is established that during the process of precipitation with the aid of ammonia, iron and titanium, being in the form of complex ammonium-fluo-salts are almost not precipitated and the content of these admixtures in the obtained zirconium dioxide is much smaller than that in the initial potassium fluozirconate. This is confirmed by the data shown in Table I.

Table I. The Content of Admixture of Iron and Titanium in the Initial Potassium Zirconate and Zirconium Dioxide

No. of experiment	*Initial potassium fluozirconate*		*The obtained zirconium dioxide*	
	Fe %	*Ti %*	*Fe %*	*Ti %*
1	0.032	0.012	0.006	0.005
2	0.032	0.012	0.005	0.005
3	0.031	0.012	0.004	0.005
4	0.033	0.017	0.005	0.005
5	0.030	0.012	0.004	0.005

Chemical analysis of pure zirconium dioxide admixtures content (in per cent) is: HfO_2, less than 0.01; Fe_2O_3, 0.005–0.006; TiO_2, less than 0.005; MnO_2, 0.001–0.002; WO_3, less than 0.001; CoO, less than 0.0001; NiO, less than 0.0003; CuO, 0.0013–0.0015; Ag_2O, less than 0.0003; CdO, less than 0.00003; Li_2O, 0.004–0.006; B_2O_3, less than 0.00001; K_2O, 0.008–0.01.

SUMMARY AND CONCLUSIONS

1. Purified zirconium dioxide is obtained with a hafnium content less than 0.01% from potassium fluozirconate free from hafnium.

2. Separation of hafnium from zirconium was accomplished through fractional crystallization of potassium fluozirconate. This method can be used for obtaining potassium fluozirconate from zircone (baddelevite) by sintering with potassium fluosilicate.

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Methods of Separating Zirconium from Hafnium and Their Technological Implications

By F. Hudswell and J. M. Hutcheon,* UK

The classical inorganic chemical problem of separating hafnium from zirconium has acquired a technological significance with the advent of nuclear power. Zirconium is of interest here not only, as elsewhere, because of its useful corrosion resistance but because of its almost unique combination of this feature with a low thermal neutron capture cross section (0.18 barns). Hafnium, however, which is so tenaciously associated with zirconium in natural forms has the very high capture cross section of 120 barns. Thus the corresponding value for a hafnium-zirconium mixture in the naturally occurring proportion of about 2.5 per cent by weight would be about 1.6 barns; this is no longer attractive. A high premium is therefore placed on separating these two elements and under this stimulus several methods have been developed in various countries. The purpose of this paper is to describe some of the processes studied in the UK, to relate them to the general background of the extraction metallurgy of zirconium and to attempt an assessment of their technological significance.

SEPARATION METHODS

Fractional Distillation of the Complexes Formed by the Tetrachlorides with Phosphorus Oxychloride

It has been known for many years that the tetrachlorides of zirconium and hafnium form additive compounds with phosphorus pentachloride and oxychloride and that some degree of separation of zirconium from hafnium is possible.[1]

A further investigation[2] of this method was embarked upon at A.E.R.E., Harwell and use was made of information which came to hand,[3] during the course of this work, from the USA. The $POCl_3$, additives were studied in both cases.

With an urgent demand for 500 gm of zirconia containing less than 0.1 per cent of hafnia this treatment seemed most certain, at that time, to yield the desired product.

Starting with zirconia as the raw material, the additive compounds were prepared by refluxing with phosphorus pentachloride, in slight excess, according to the reaction:

$$3(Zr,Hf)O_2 + 6PCl_5 = 3(Zr,Hf)Cl_4 \cdot 2POCl_3 + 4POCl_3$$

The additive compounds remained when the free $POCl_3$ and excess of PCl_5 were distilled off.

The fractional distillation of this product was carried out in the apparatus shown in Fig. 1. The apparatus has a boiler capacity of 1 litre, a column 60 in. long and ¾ in. diameter packed with ⅛ in. glass helices and surrounded by a heating jacket.

The charge was about 1000 gm of the additive compounds containing 1.5% by weight of HfO_2 in ZrO_2.

Using a boil up rate of 800 gm an hour, with a take-off rate (intermittent) of 20 gm an hour and a distillation time of 30 hours, a product of 400 gm of $3ZrCl_4 \cdot 2POCl_3$, or 121 gm of ZrO_2 (containing 0.075% of HfO_2) was obtained. The objective was achieved, therefore, in four such distillations.

It is preferable to remove impurities other than hafnium by a prior distillation in which the first and last small fractions are rejected.

In passing it is of interest to remark on the greater volatility of the hafnium compound relative to the zirconium compound; the compound of higher molecular weight is in fact more volatile. This phenomenon also appears among the alkoxides and is, in fact, widespread among other compounds. An explanation has been given in terms of statistical thermodynamics.[4]

Fractional Distillation of Alkoxides

This work has been pioneered by Wardlaw, Bradley and their collaborators at Birkbeck College, University of London, and is still being pursued on a laboratory scale.

The alkoxides are most suitably prepared by the action of dry ammonia on a suspension of the pyridinium zirconium (hafnium) hexachloride in a dry mixture of iso-propanol and benzene. The products are the tetra-isopropoxides with alcohol of crystallisation.[5] Other alkoxides of less volatile alcohols may be obtained by refluxing this product with the appropriate alcohol.

Vapour pressure curves have been determined for a number of alkoxides prepared from pure hafnium and zirconium compounds. The indications are that the boiling point difference increases towards higher pressures but thermal decomposition sets a limit before atmosphere pressure is reached.

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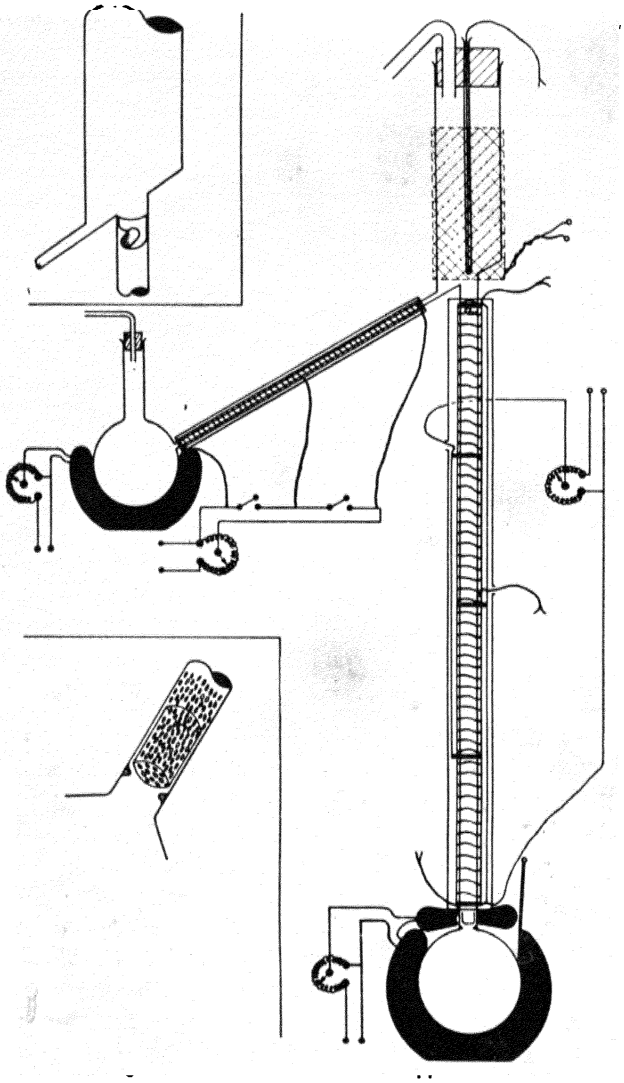


The figures below illustrate the potentialities.

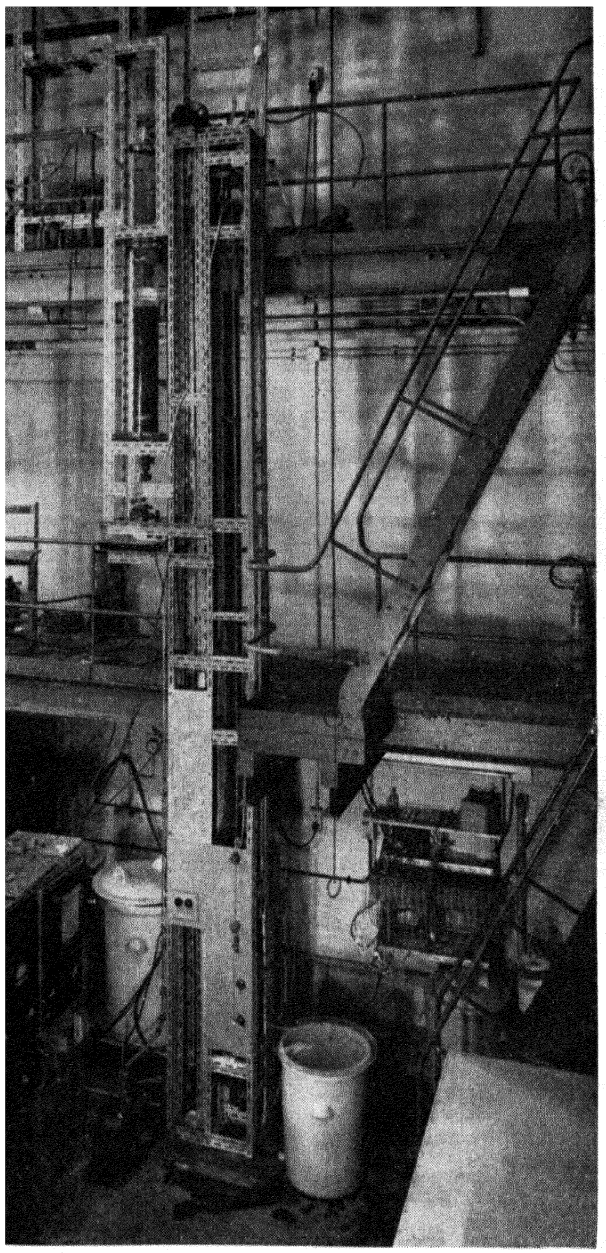
Alkoxide	*Boiling point of Zr compound at 5 mm Hg, °C*	*Boiling point of Hf compound at 5 mm Hg, °C*
Tert-butoxide	89.2	87.6
Tert-amyloxide	137.0	135.8

More recent results have shown that there is a tendency for the vapour pressure curves for a given set of zirconium and hafnium compounds to converge towards higher temperatures. This means that there will be an optimum temperature of enrichment of hafnium in the vapour phase and that the most economic operation will depend on working in the vicinity of this temperature.

Paper Chromatographic Separation

Paper chromatographic separation of these metals has been investigated and developed into a column process at the Chemical Research Laboratory, D.S.I.R., Teddington.[6, 7]

The method depends on the more rapid elution of zirconium when a wad of cellulose pulp impregnated with zirconyl nitrate is treated with diethyl ether containing 12.5 vol/vol per cent of concentrated nitric acid.



About 70% of the zirconium can be obtained, with a content of less than 0.01% HfO_2 (calculated on ZrO_2), starting with 200 gm of zirconyl nitrate, $ZrO(NO_3)_2 \cdot 2H_2O$ (or 92 gm ZrO_2).

For operation on the large scale this method would appear to have the disadvantages of inflammability and explosion risks, batch processing with consequent high costs for labour and analytical control, as well as incomplete yield. On the credit side the zirconium product is very pure and is sharply separated from elements other than hafnium; pure hafnium salts also should be recoverable.

Cation Exchange Process

Lister and MacDonald[8] have described the laboratory development of this process. They adsorbed zirconium and hafnium together in a thin layer at

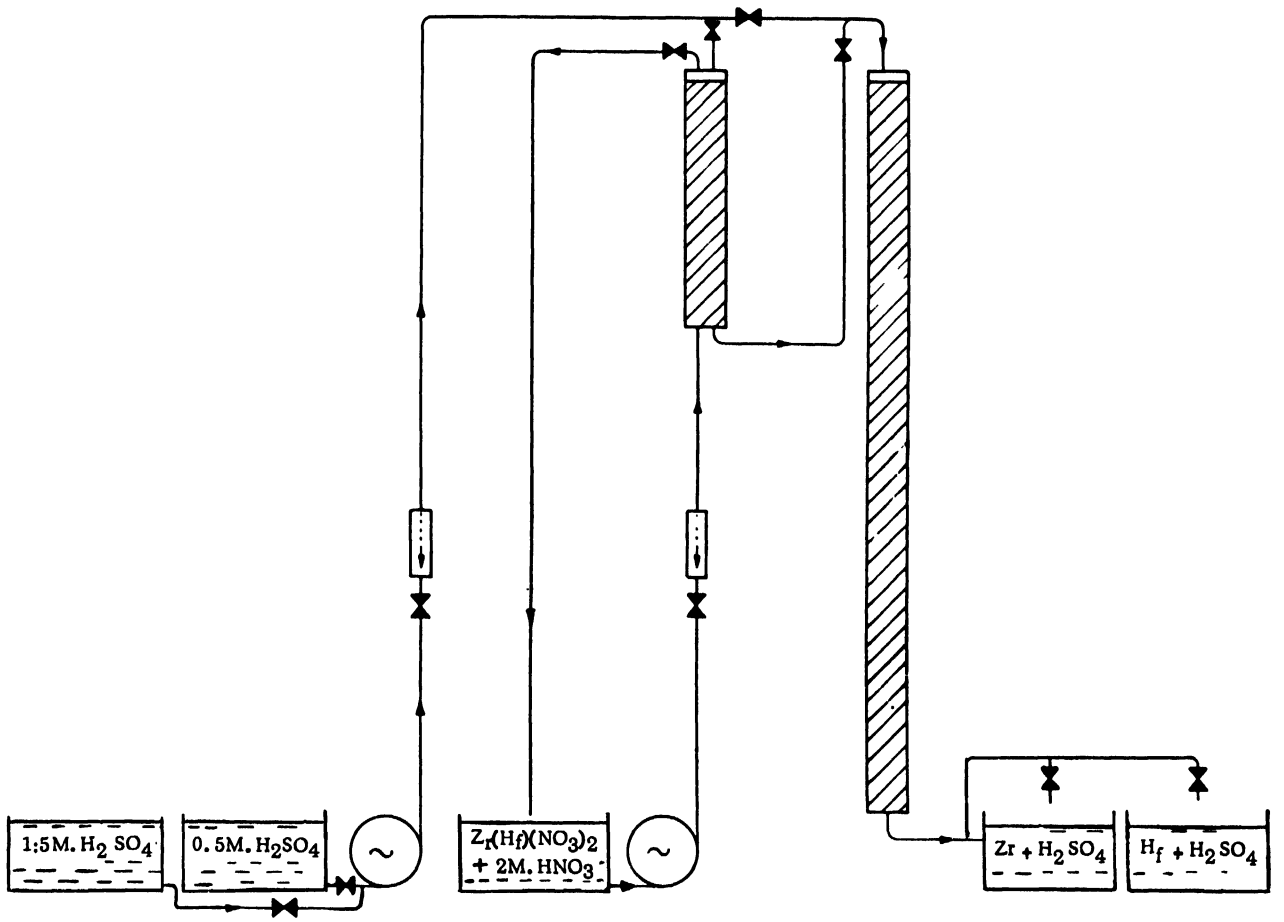


Figure 3. Hf/Zr separation ion-exchange process flow diagram (schematic)

the top of a column of cation exchange resin ZK 225 and subsequently eluted the adsorbed cations with 0.5*M* sulphuric acid. The zirconium moved down the column ahead of the hafnium and, with sufficient column length 95–98% of the zirconium was recovered containing less than 0.01% hafnium. The hafnium was then eluted rapidly with 1.5*M* sulphuric acid.

This process is quite analogous to the citrate elution process used by Spedding[9] for the separation of rare earths. The resin serves only as an inert substrate for the cations and the separation results from the different complex-forming tendency of the ions HfO^{2+} and ZrO^{2+} with sulphuric acid. Any difference in affinity of the two ions for the resin is very slight and plays no significant part in the separation.

For the production of kilogram quantities of pure zirconium and small quantities of hafnium for experimental purposes, this method has been scaled up directly. Figure 2 is a photograph of the equipment used in its final form and Fig. 3 is a schematic drawing. The left-hand "impregnation" section contained 13.3 kg (dry weight) and the right-hand "main column" 21.3 kg (dry weight) of resin. The impregnation section consists of standard lengths of 6 in. diameter Pyrex tubing and the main column is fabricated from perspex sheet with one face kept smooth and free from flanges.

In operation zirconyl nitrate solution in nitric acid† is pumped continuously from a storage vessel upwards through the impregnation section at a flow rate of about 60 l/hr, thus maintaining the bed in a "fluidised" condition. The solution overflows back to the storage vessel. This cycling is continued for about 30 hours by which time about 60% of the zirconium in the feed solution is adsorbed on the resin.

The unadsorbed zirconium is precipitated with ammonia and redissolved in nitric acid with fresh zirconyl nitrate for subsequent runs.

During the impregnation, the main column is "conditioned" with 0.5*M* sulphuric acid. At the end of the impregnation the side column is backwashed successively with 2*M* nitric acid and distilled water. 0.5*M* sulphuric acid is then flowed at 8 l/hr down the side column and the main column in series and the effluent collected and precipitated. When the hafnium content rises to an unacceptable level the eluant is changed to 1.5*M* sulphuric acid, which removes the remaining zirconium and hafnium from the column very rapidly. The total elution time is approximately 130 hours. In later runs the later stages of elution have been carried out concurrently with the impregnation for the next run.

† Volume 133 liters Zr, ca 17 gm/l HNO_3 2*m*.

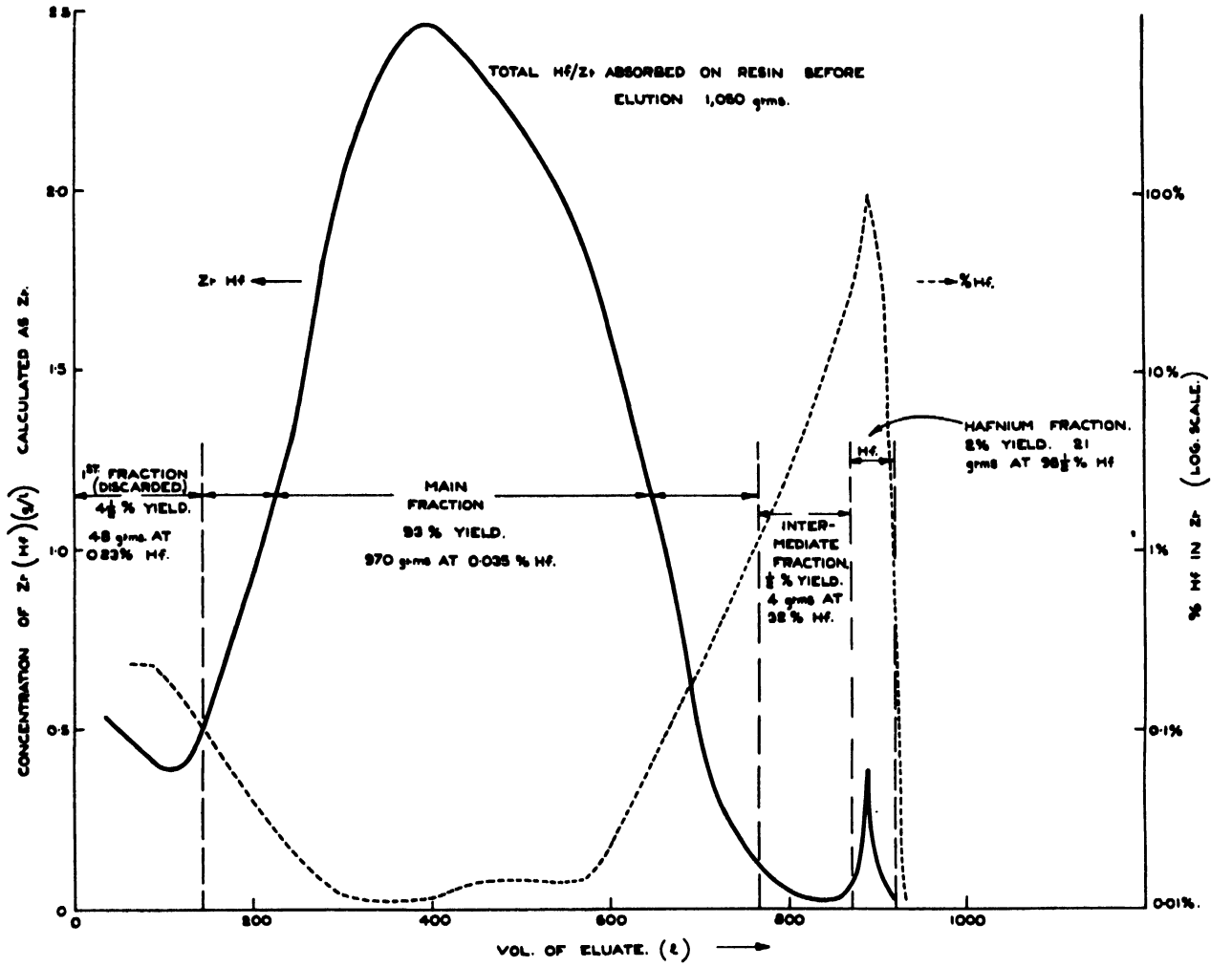


Figure 4. Concentration and purity of zirconium in eluate for a typical run

In the development of the process the feed solution was "seeded" with Hf^{181} tracer and effluent was monitored for hafnium by a flow counter measuring γ-activity, and by spectrographic analysis. The automatic sample collector for taking samples at fixed time intervals can be seen at the right of the photograph. Also an end-window counter automatically traversed the entire length of the main column in both directions once per hour. A "profile" of the hafnium activity on the column was thus drawn every hour on a recorder chart.

In later runs when the pattern had been established the column was operated on a fixed volume cycle and pre-arranged fractions were treated separately.

Figure 4 is a record of a typical run in which it will be seen that *93%* of the zirconium adsorbed on the resin was obtained at a purity level of 0.035% hafnium and in addition 21 gm were obtained of a hafnium-rich fraction containing 98½% hafnium.

This process gives very pure zirconium and also usefully rich hafnium and intermediate fractions which readily lend themselves to further concentration on a small column.

The over-all throughput rate, however, for material of acceptable quality corresponds to about 0.05 gm/hr–cm^2 equipment cross section, which is much too slow for large-scale production.

Liquid-Liquid Extraction Using Tributyl Phosphate

Tributyl phosphate ["TBP"-$PO(C_4H_9O)_3$] is known to form liquid complexes with a number of heavy metal cations and it has therefore been used as a complexing solvent in liquid-liquid extraction.

For zirconium nitrate in moderately concentrated solution containing free nitric acid, an equation may be formally written

$$ZrO^{2+} + 2H^+ + 4NO_3' + 2TBP \rightleftharpoons Zr(NO_3)_4 \cdot 2TBP$$

In the absence of adequate knowledge of the forms of the zirconium species present or of the activity coefficients at the operating concentrations this equation has not been quantitatively confirmed but it serves adequately to give a qualitative picture of the observed behaviour. Writing the equilibrium constant in mass terms, we have

$$K = G\frac{[Zr(NO_3)_4 \cdot 2TBP]}{[ZrO^{2+}]\,[H^+]^2\,[NO_3^-]^4\,[TBP]^2}$$

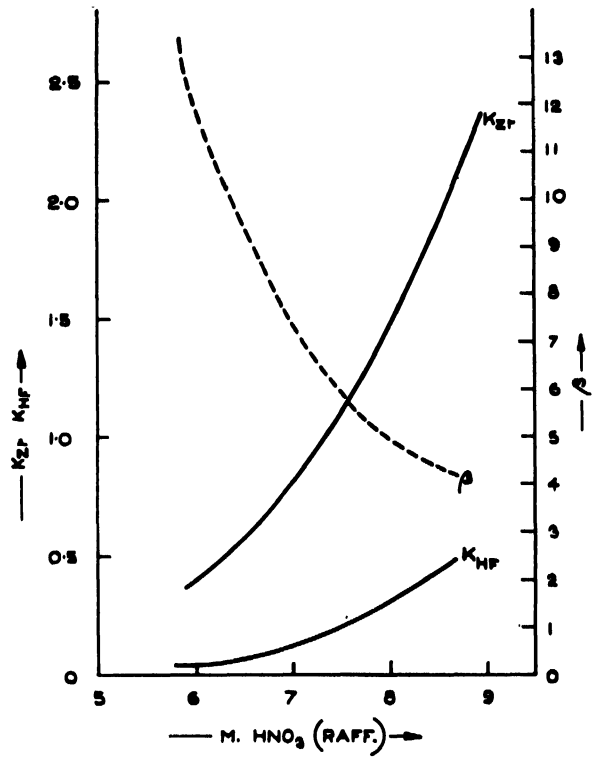


Figure 5. Partition data for 20% TBP at approx. 10 gm/l Zr feed

the activity coefficients being collected into the term G. Hence the zirconium partition coefficient is

$$K_{Zr} = \frac{K}{G}[H^+]^2[NO_3^-]^4[TBP]^2$$

Thus, ignoring for the moment any variation with concentration of the activity coefficient term G, we should expect extraction a to be favoured by increase in acidity, total nitrate concentration and TBP concentration. The operative TBP concentration is that of the free TBP, which will of course be reduced from that in the original solvent owing to combination with zirconium. In this way the over-all zirconium concentration will affect K_{Zr}.

If the zirconium is supplied as zirconyl nitrate, an apparent concentration effect on the distribution of zirconium would also be expected owing to the variation of nitrate ion concentration. Lastly, the term G will depend on concentration. The partition coefficient K_{Zr} would therefore be expected to show a complex dependence on the zirconium concentration.

Figure 5 shows the variation of K_{Zr} and K_{Hf} with nitric acid concentration for low zirconium concentrations, the organic solvent being 20 vol % TBP/kerosene. It will be seen that for efficient extraction quite high acidities are necessary with a consequent fall in the separation factor β.

The use of a centre-feed column, however, with high nitric acid concentration in the extraction (lower) section and lower acidity in the stripping (upper) section wherein hafnium is washed back into the aqueous phase, gives efficient yield and separation. Figure 6 shows a suitable flowsheet which

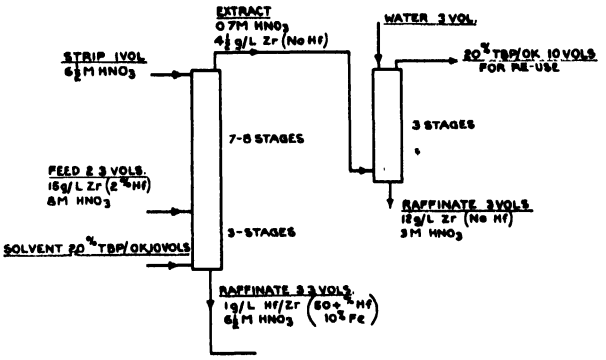


Figure 6. Flowsheet for Hf/Zr separation using 20% TBP solvent

has been operated in a 1-in. diameter column. With these conditions 94 per cent of the zirconium was recovered at a hafnium content of 0.04 per cent.

The throughput of this system is low, mainly because of the low concentration involved. In the 1-inch experimental column, the maximum practicable operating flow rate was 50 ml TBP/kerosene per minute, corresponding to a mass flow of ca 2.5 gm zirconium/hr/cm^2. This is better than the throughput of the ion-exchange process by a factor of 50 and would permit of a nominal production of 100 tons zirconium per year from something less than 0.7 m^2 of column area but is capable of further improvement.

The process also suffers from an excessive use of reagents. Thus approximately 80 moles of nitric acid pass through the columns for every mole of zirconium produced and the recovery of this nitric acid would be a disproportionately large item in the costs of the process. Recycle losses on the solvent would probably also be high owing to the high solvent/aqueous ratio.

Further work was therefore directed towards increasing the concentration of zirconium in the solvent phase. This concentration was limited in the earlier experiments by the formation of a third phase in the solvent layer owing to the limited solubility of the zirconium nitrate/TBP compound in kerosene. This situation could be improved by changing the diluent to xylene, in which the zirconium compound is more readily soluble. When all the TBP in a 20% solution is combined with zirconium, however, the solution is still only 0.36M in zirconium. To increase this the TBP concentration must be raised, thus increasing the viscosity of the solvent layer; an upper limit is therefore set by difficulties in operating the contactors. As a suitable compromise 50% TBP/xylene has been used.

Increase in zirconium concentration also brings about a marked fall in the zirconium partition coefficient as is instanced by Fig. 7 which shows the variation of K_{Zr} with zirconium concentration for 50% TBP/xylene for an aqueous feed 5M in nitric acid. Although the zirconium coefficients are much greater than with the 20% TBP solvent at comparable acidity, they are still too low for convenient use. To give suitable working conditions the

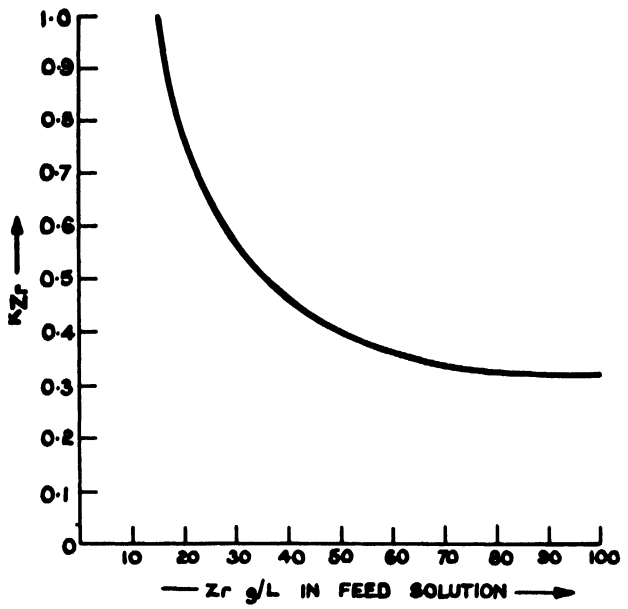


Figure 7. Variation of KZr with increasing Zr concentration at a constant 5M NHO_3 in raffinate after equilibriation

nitric acid concentration has therefore been increased further. The alternative procedure of "salting out" from the aqueous solution by adding e.g., ammonium nitrate and thus increasing the total nitrate concentration in the aqueous layer creates more difficulties in feed preparation and reagent recovery than it solves. The flowsheet finally developed is shown in Fig. 8.

This, on the basis of a similar column to that previously used gives about 10 gm Zr/hr/cm^2—a further increase in throughput by a factor of 4.

Moreover the nitric acid required has now been reduced to approximately 10 moles HNO_3 per mole Zr.

RELATION OF HAFNIUM-REMOVAL METHODS TO THE TOTAL ORE-METAL SCHEME

Methods 1, 3–5

These methods all start and finish essentially with the hydrous zirconium oxide. This compound does not appear at all, however, in the normal (Kroll) extraction route shown in Fig. 9A. Thus two problems are posed—preparation of the hydrous oxide from zircon sand and its reduction to metal. The reduction can be performed relatively simply through the chloride as in the Kroll process. The hydrous oxide may be ignited to the oxide, which is then briquetted with a carbonaceous binder. The briquettes are chlorinated and the anhydrous chloride which distils over is condensed. Another possible tions by D. C. Bradley and W. Wardlaw of Birkbeck route has been indicated[10] by the recent investiga- College, London. These authors have shown that chlorination of zirconium oxychloride hydrate to the tetrachloride can be brought about by refluxing with thionyl chloride at atmospheric pressure. The reaction from the oxychloride goes very much more easily than the parallel reactions for the ignited or hydrous oxides which have been investigated by Hecht and co-workers.[11] Alternatively the hydrous oxide might be used as starting point for other zirconium compounds (e.g., oxide or fluorozirconate) which it has been proposed to reduce[12] to give the metal.

The hydrous oxide has been prepared[13] by fusing zircon sand with caustic soda to give a "frit"—a mixture of sodium zirconate and silicate. This was washed with water when the soluble sodium silicate was removed and the zirconate hydrolysed to an impure hydrous zirconium oxide, which was readily soluble in dilute acids.

Experiments have been made with such a "washed frit" as feed material to the TBP process. The only difficulties arose from the small amount of silica which is not removed by washing. Some of this is finely divided insoluble material which appears to be the source of serious emulsification in the contactors. A preliminary filtration after the addition of calcined Kieselguhr has been found effective in curing this trouble. The second difficulty derives from dissolved silica which causes the aqueous stream from the first extraction column to "gel" after a few hours standing. Since this stream contains about 80% of the nitric acid fed to the first column and should go to a nitric acid recovery stage, a satisfactory solution of this difficulty is significant to the economics of the process.

Thus a suitable combination of these processes gives a "wet extraction" route from the crude zircon sand to the purified hafnium-free hydrous oxide from which a number of possible routes exist to the metal. The wet extraction scheme is shown in Fig. 9B.

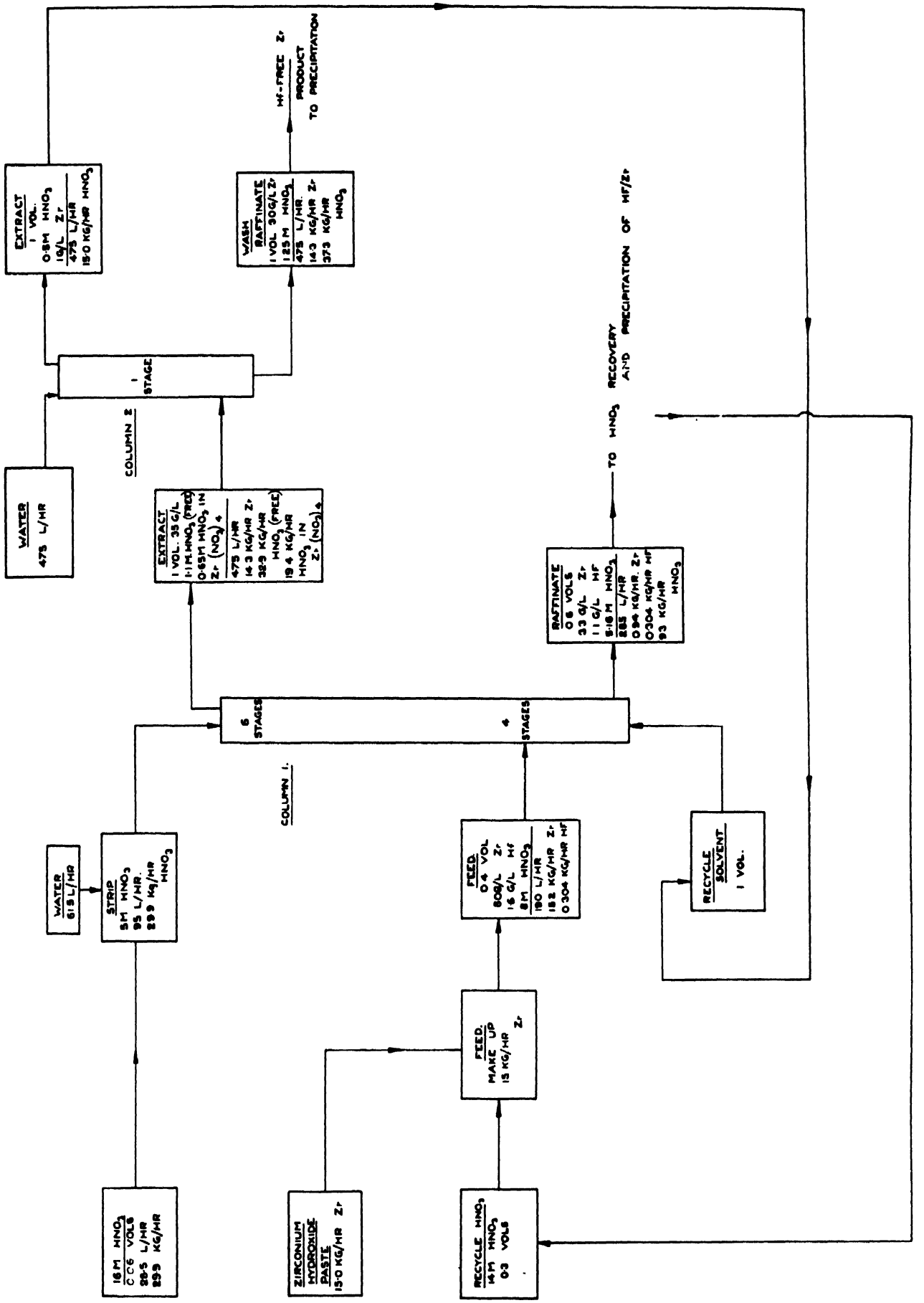
Method 2

The alkoxide method starts essentially from zirconium tetrachloride and finishes with an alkoxide which, so far at least, has been converted to oxide. This process therefore requires a change from the anhydrous tetrachloride to the hydrous oxide and back to the tetrachloride, which is not attractive economically. Moreover the cost of the zirconium by the time it has been made into tetrachloride is relatively high and the separation process would therefore have to be very efficient to overcome the disadvantages of starting with an expensive material. On the other hand it is not essential to isolate the tetrachloride since this can be prepared (by the method of Bradley and Wardlaw described above) from the oxychloride. In this light the alkoxide separation process is also a "wet" process.

Comparative data for the processes described in this paper are shown in Table I.

CONCLUSION

The general conclusion from the above discussion is that the separation methods described fit more readily into a caustic soda ore-extraction metallurgy


EXTRACT
1 VOL.
0·8M HNO3
19/L Zr
475 L/HR
15·0 KG/HR HNO3
WASH RAFFINATE
1 VOL 30G/L Zr
1·25 M HNO3
475 L/HR.
14·3 KG/HR Zr
373 KG/HR HNO3
Hf-FREE Zr PRODUCT TO PRECIPITATION
1 STAGE
COLUMN 2
WATER
475 L/HR
EXTRACT
1 VOL. 35 G/L
1·1 M HNO3 (FREE)
0·65M HNO3 IN
Zr (NO3)4
475 L/HR
14·3 KG/HR Zr
38·9 KG/HR
HNO3 (FREE)
19·4 KG/HR
HNO3 IN
Zr (NO3)4
TO HNO3 RECOVERY AND PRECIPITATION OF Hf/Zr
RAFFINATE
0·6 VOLS
3·3 G/L Zr
1·1 G/L Hf
5·18 M HNO3
285 L/HR
0·94 KG/HR. Zr
0·304 KG/HR Hf
93 KG/HR HNO3
6 STAGES
4 STAGES
COLUMN 1.
WATER
61·5 L/HR
STRIP
5M HNO3
95 L/HR.
29·9 Kg/HR HNO3
FEED
0·4 VOL
80G/L Zr
1·6 G/L Hf
8M HNO3
190 L/HR
18·2 KG/HR Zr
0·304 KG/HR Hf
RECYCLE SOLVENT
1 VOL.
FEED.
MAKE UP
15 KG/HR Zr
16M HNO3
CCE VOLS
28·5 L/HR
29·9 KG/HR
ZIRCONIUM HYDROXIDE PASTE
15·0 KG/HR Zr
RECYCLE HNO3
14M HNO3
0·3 VOLS

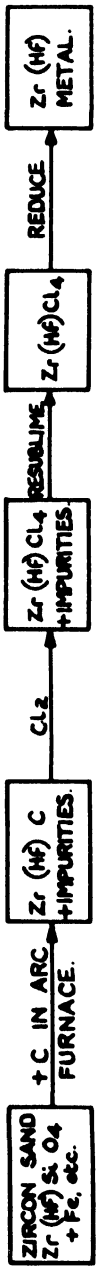


Figure 9A. Kroll process for commercial Zr metal

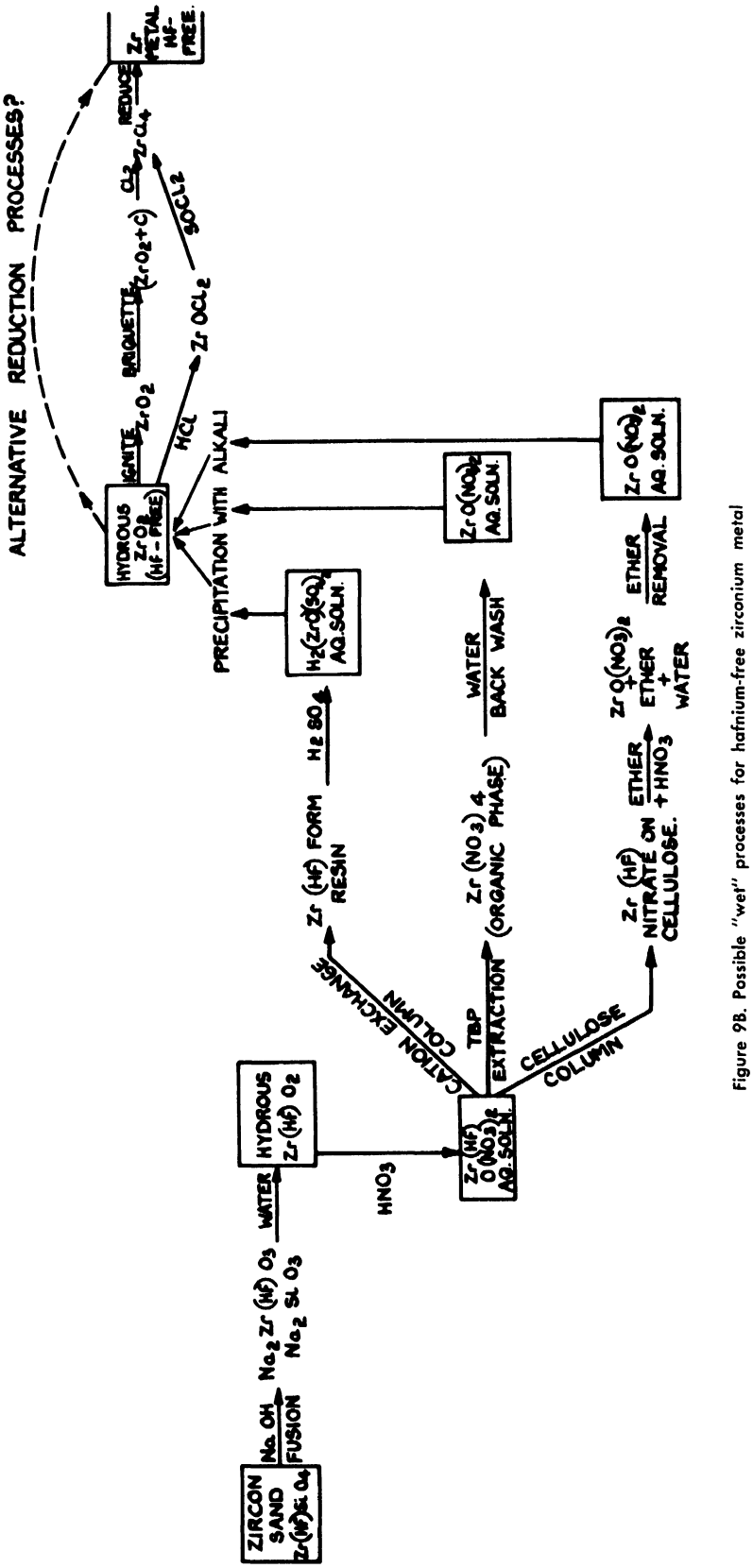


Figure 9B. Possible "wet" processes for hafnium-free zirconium metal

Table I. Comparative Data for the Separation Processes

	1. *$POCl_3$ addition*	2. *Alkoxides*	3. *Paper chromatography*	4. *Ion exchange*	5. *TBP extraction*
Source of separation	Heat for distillation (only partly recoverable)		Cellulose (solid substrate) + HNO_3 (difficult to recover)	Exchange resin (solid substrate recoverable) + H_2SO_4 (difficult to recover)	TBP/Xylene (recoverable) + HNO_3 (mostly recoverable)
Separation factor	1.14	1.01–1.02 (at 160°C)	Probably high	~4	~4
Purity obtained in experimental work	<0.1% Hf	—	0.01% Hf	0.02% Hf (90% recovery)	0.03% Hf
Throughput of pure Zr	3 gm/hr/cm²	Low, owing to the necessarily high reflux ratio	0.05 gm/hr/cm²	0.05 gm/hr/cm²	10 gm/hr/cm²
Chemical form of Zr fed to separation equipment	Dry ZrO_2	$ZrOCl_2 \cdot 8H_2O$, Hydrous ZrO_2 or $ZrCl_4$	Hydrous ZrO_2 (impure)	Hydrous ZrO_2 (impure)	Hydrous ZrO_2 (impure)
Auxiliary reagents	PCl_5	Pyridine, benzene, alcohols, NH_3	Ether	HNO_3	None
Plant materials	Only glass has been used so far	Glass	Glass or stainless steel	Glass or rubber-lined steel	Stainless steel
Type of operation	Continuous	Intended to be continuous	Batch	Batch	Continuous
Operational difficulties	Anhydrous conditions essential	Anhydrous conditions essential	Fire risks	Simple to operate	Slight fire hazard from xylene, contactor problems arise from viscosity, low density difference, and emulsification
Chemical form	$ZrCl_4/POCl_3$	$Zr(OBu)_4$+BuOH, or Zr (OisoAm)$_4$+ iso AmO H	$ZrO(NO_3)_2$ in ether + HNO_3	$ZrOSO_4$ in N H_2SO_4	$ZrO(NO_3)_2$ in aqueous 0.5M HNO_3

than into the established carbide process. Their position would be considerably strengthened if for any reason alternatives to the chloride reduction route became attractive.

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The Use of Radioactive Isotopes in the Study of the Analytical Chemistry of Zirconium and Hafnium

By N. S. Poluectov, Ukrainian SSR

In spite of more than 150 years having elapsed since the discovery of zirconium, the analytic chemistry of this element to this day is comparatively little explored. Till recently zirconium was determined by rather protracted methods, mainly founded on weighing. There were very few data on the properties of the water solutions of salts of this element which are so important for analytic chemistry, on the extent of their hydrolysis in various conditions, on zirconium's iones capacity for complex-forming, etc. It is but lately that certain investigations have been made in the research of sufficiently quick and simple colorimetric and volumetric methods for determination of zirconium.

As regards hafnium, its chemical properties being similar to those of zirconium, to this day no direct chemical methods are known by which it may be determined in the presence of the latter. In this view the roentgenospectral and optic spectral methods requiring complicated apparatus (the latter has been but recently developed and proved to be more accessible) usually are made use of. The indirect chemical methods, based on differences in the atomic weights of elements, are extremely complicated and of limited application.

With the increasing need for pure preparations of zirconium and hafnium, the necessity arises to find simple, quick and useful for practice methods for determination of these elements. It was necessary to develop the colorimetric and volumetric methods for estimation of the quality of ore, and also to provide methods for extracting or concentrating hafnium out of preparations of zirconium.

In the course of the present work it was found useful to apply the method of labelled radioactive tracer for controlling the distribution of zirconium and hafnium through the various stages of analysis. This method brings quick results in cases when they may not be obtained in other ways.

The present paper contains the results of investigations conducted during 1952–1954 with application of radioactive isotopes, aimed at working out a method for determination of zirconium in ores, and likewise methods for separating hafnium by means of distributive chromatography on paper and by counter-current extraction.

Original language: Russian.

1. COLORIMETRIC DETERMINATION OF ZIRCONIUM IN ORES

The object of the present work is to develop a simple method of colorimetrical determination of zirconium which would ensure sufficient precision in the determination of both zirconium and hafnium. Further on, it was desirable to reduce as far as possible the number of operations involved in separating zirconium from alien elements. The best way of doing this would be a method enabling the determination of zirconium without separating it previously out of other elements; in case of its low content, preliminary concentration of zirconium might be needed. The papers give a number of methods for colorimetric determination of zirconium, for instance with alizarin,[1] with dimethylaminoazophenylarsonic acid,[2] with quercetin[3] and alizarin red.[4-6]

Some of these methods are either inconvenient,[1,2] or insufficiently explored as to interference with such alien metals as, for instance, tantalum or niobium, which may be present in the sample.[3-6] Therefore, it was desirable to conduct a comparative assay to determine fitness of various reagents for colorimetric determination of zirconium.

As a result of the work completed it was found that the most practicable reagents for the determination of zirconium are dyes having hydroxile groups in orthoposition to each other, or in the quinone group. These reagents may also have 2 hydroxile groups in orthoposition to the azo-group (in azo-dyes) in various nucleus (benzole or naphthaline). It was pointed out in papers that the organic reagents containing O-dioxyphenyl group become capable to react with zirconium.[7] To the fitting reagents belong also azo-dyes containing an arseno group in orthoposition to the azo-group in one aromatic nucleus, and a hydroxile atom group in the same position in the other.

Table I shows some of the explored reagents with figures on their sensitivity. The latter is characterized by the value of light extinction measured with a suitable light filter and recalculated for 10 μg of zirconium in 10 ml, the length of the cells being 10 mm. The ability of the compounds marked as No. 4 and 5 in the table to react with zirconium has been mentioned earlier.[4-6,8]

The next stage was the studying of the relationship between the reagents and other elements which

can be present in ores. It was found out that the most sensitive reagent—phenylfluorone—is the least specific, as it reacts with salts of iron(III), titanium, molybdenum, tungsten, tin(IV), and to a smaller extent with niobates and tantalates. "Arsenazo" and alizarin red proved to be the most suitable. "Arsenazo" reacts feebly with niobium, tantalum and molybdenum. Alizarin red gives a feeble reaction to titanium as well. Large quantities of ferric salts somewhat hinder the determination of zirconium.

To eliminate this obstacle, the iron(III) is to be reduced to a bivalent state.

The influence of other elements which at high concentrations hinder the determination of zirconium, could not be eliminated either by changed acidity or by selection of respective camouflaging means as all the tested complex-formers camouflaged first of all the very zirconium. But it was established however, that under definite circumstances complexone-111-ethylenediamine-tetraacetic acid, which camouflages zirconium in colour reactions, leaves untouched the weakly coloured compounds of other metals. Further on, the possibility was found to eliminate hindrances at the determination of zirconium, on the part of the other elements. It consisted in the following: the solution of the sample with the reagents is subjected to photocolorimetric operation, the blind sample solution being the very solution in which complexone camouflages zirconium. The extinction of light by coloured compounds of alien metals, if the work is conducted on a double-armed colorimeter, is optically deducted from the extinction of light by the sample solution and in this way consistent results are obtained for zirconium. For example, the presence of 1 mg of titanium or 0.1 mg of niobium at usual colorimetry with "arsenazo" increases the actual amount of zirconium by 5–6 micrograms its content being 40 μg. The presence of 1 mg of titanium or niobium does not cause any serious errors, if at colorimetric operation the use is made of sample solution holding reagents and complexone as a means for control. When 200 μg of zirconium are tested with alizarin red by the usual method, the presence of 1 mg of niobium causes an error of + 30 μg; 1 mg of titanium—an error of + 50 μg of zirconium. When the use is made of complexone, the presence of even 3 mg of niobium and 20 mg of titanium does not influence the results.

Table I. Reagents for Colorimetric Determination of Zirconium

No.	Reagents	Acidity of solution, HCl, N	Change in color when adding salts of zirconium	Realtive sensitivity
1.	Phenylfluorone	0.15–0.85	yellow-red	1.05
2.	4-nitrobenzolazo-pyrocatechine	0.5	the same	0.15
3.	4-sulfo-2-naphthole-1-azoresorcine	0.1–0.4	brownish-yellow-pink	0.13
4.	2-arsonobenzole-1-azo-2-chromotropic acid (arsenazo)	0.25	pink-violet	0.11
5.	Alizarin red	0.5	yellow-red	0.05

The application of the above-mentioned method of colorimetric operation made it possible to work out the following methods for analysis of zirconium ores. The sample is melted with a mixture of borax and soda, the melt being dissolved in water and the precipitate of hydroxides filtered. After washing, the precipitate is dissolved in hydrochloric acid calculated to produce a solution of definite acidity; then it is diluted to a definite volume and an aliquot of it is colorimetrically determined. This method ensures fast determination of zirconium in ores with a zirconium content of 0.2% and more, the sample of ore being 500 mg.

To determine zirconium in cases of its lower content in the ore (hundredths and thousandths of %) direct colorimetry of the tested solution by the above method is hardly suitable. In this case the zirconium must be extracted and concentrated prior to its colorimetric determination.

When working out a method for concentrating zirconium a radioactive isotope of hafnium-181 was employed instead of the zirconium-95, owing to the greater simplicity of operations with Hf^{181} (absence of an affiliate isotope of another element as in the case of Zr^{95}). The application of the method of marked atoms made it easier to follow the distribution of zirconium among phases at various stages of analysis. Due to the similarity of the chemical properties of zirconium and hafnium, and to the prevailing content of zirconium, as compared to that of hafnium, the behaviour of the isotope Hf^{181} corresponded to the behaviour of zirconium.

In the first place a suitable precipitant was chosen for precipitating microgram quantities of zirconium, provided its simultaneous separation out of the present elements. It was found out that phenylarsenic acid in 1*N* solution of hydrochloric acid could precipitate as much as 25 μg of zirconium. The efficiency of precipitation in this case reached 94–95%. The presence of hydrogen peroxide ensures the separation of zirconium from tantalum, titanium, niobium and other metals, and also, to a great extent, from tin. No suitable collector was found. To determine zirconium colorimetrically it is necessary to find a method to dissolve it after it is concentrated out of phenylarsonate sediment. After a series of experiments it was found possible to process the phenylarsonate precipitate on the filter with ammonia, and then with hydrochloric acid. Under the influence of ammonia zirconium phenylarsonate decomposes with the formation of a hydroxide, which subsequently being processed with hydrochloric acid produces a solution of zirconium oxychloride, suitable for colorimetric determination. Testing by means of the

radioactive isotope of hafnium showed, however, that in this case a part of the zirconium (up to 7%, the total zirconium being 100 μg) passes into the alkaline filtrate, possible, in the form of a colloid solution. At the same time a part of the zirconium from 5 to 12%—after processing it with hydrochloric acid—remains on the filter and thus is lost. On this account respective modifications were introduced into the course of the analysis. From the ammoniacal filtrate the zirconium was additionally precipitated on aluminium hydroxide. To dissolve zirconium completely, the filter was additionally processed with oxalic acid, which converts the zirconium into a complex anione not absorbed by the filtering paper.

Experiments conducted on artificial mixtures with a zirconium content of 0.5–0.1 mg (0.1–0.02% in relation to the whole amount of metals present), with the addition of the radioactive isotope of hafnium, demonstrated that in these conditions 94–97% of the zirconium content in the solution passes into the colorimetric solution.

After the introduced modifications, the whole procedure of the analysis consisted of the following operations:

(1) A sample is frited with a mixture of borax and soda, the mixture dissolved in water, the precipitate filtered off and washed.

(2) The precipitate is then dissolved in hydrochloric acid and after the addition of hydrogen peroxide the zirconium, from the obtained solution, 1 *N* to the hydrochloric acid, is precipitated with phenylarsonic acid.

(3) After settling, the precipitate is filtered off, washed and processed on the filter with ammonia, deprived of its carbonate ion. To the ammoniacal solution is added 0.5 ml of the aluminium chloride solution (6 mg/ml Al_3) and the whole is again passed through the same filter. In conclusion the precipitate is several times washed with a 2% solution of sodium chloride.

(4) The precipitate is dissolved on a filter in 6.7 ml of hot 5 *N* hydrochloric acid; the filter, after being twice washed with water, is processed with 2 ml of hot oxalic acid and again washed with water. Before the beginning of colorimetric determination the oxalic acid in the solution must be destroyed, which is achieved by processing it with potassium permanganate and boiling. The excessive permanganate is reduced by a drop of hydroxylamine hydrochloride solution.

(5) The solution being cooled and diluted to 25 ml, its zirconium content is determined, for which an aliquot of the solution is mixed with the reagent (definite acidity being observed) and the light extinction is assayed on a photocolorimeter with a yellow light-filter (maximum passage 570 mμ).

To examine the degree of zirconium dissolution in colorimetric solution, the isotope of hafnium-^{181} was added to the ore samples in amounts to 1–2 μc; its distribution in the stages of analysis was determined by measurements of its activity.

The results are given in Table II.

As it can be seen from the table, 94.5–97% of the present zirconium passes into the colorimetric solution, which in cases of its low content may be considered sufficient. The control analysis conducted on a number of samples containing 0.01–0.2% of zirconium oxide showed a satisfactory coincidence (within the limits of 0.01–0.02%) with the data of the spectral method.

The results of analysis of zirconium ores with additions of zirconium are given in Table III. Colorimetry was fulfilled with the aid of the "arsenazo" reagent.

The difference between the found and total zirconium content only in one case exceeds 0.01%, the error, however, being less than 7% (relative).

In conclusion it seemed interesting to us to check the distribution of niobium and tantalum in the course of the analysis, considering the possibility of interference on their part during the colorimetric determination of zirconium. This was fulfilled by addition of a definite quantity (2–3 μc) of radioactive isotope (Nb^{95} or Ta^{192}) to the ore and by determining the activity of solutions obtained in the course of analysis. The zirconium content of the ore was 0.04%, 0.2 and 2.0%. The niobium and tantalum contents ranged from hundredths and thousandths of per cent to 2.2%. (In the latter case ar-

Table II. Distribution of Isotope of Hafnium-181 When Conducting Stages of Ore Analysis

No.	ZrO_2 content in sample %	Distribution of Hf^{181} during analysis: Filtrate after melting	Filtrate after phenyl arsonic acid precip.	Filtrate after processing of precipitate with ammonia	Final hydrochloric solution
1	0.0332	0	1.58	1.8	96.6
2	0.05	3.5	1.65	0.4	94.5
3	0.16	0.35	1.8	0.89	97.0
4	0.2	1.28	2.2	0	96.5
5	2.0	0.82	0.41	0.51	98.2

Table III. Analysis of Ores with Addition of Zirconium

No.	ZrO_2 content in sample, %	Added ZrO_2, %	Total ZrO_2, content %	Amount of ZrO_2 found in sample with add., %	Difference, %
1	0.02	0.05	0.07	0.069	0.001
2	0.025	0.04	0.065	0.066	±0
3	0.028	0.05	0.078	0.08	+0.002
4	0.04	0.05	0.09	0.089	−0.001
5	0.078	0.1	0.178	0.19	+0.012
6	0.09	0.05	0.14	0.148	+0.008
7	0.092	0.04	0.132	0.128	−0.004
8	0.107	0.04	0.147	0.147	0
9	0.16	0.1	0.26	0.255	−0.005

tificial additions were made to the respective ores). The results are given in Table IV.

With small amounts of zirconium, more than half of the niobium is removed already during the filtering of the solution obtained at the leaching of the borate-carbonate melt. With large amounts of zirconium, only a minor part of the niobium passes into the alkaline solution, while its greater part is precipitated with the zirconium phenylarsonate.

As to tantalum, as it is seen from the table, it is completely absent in the filtrate of the alkaline solution of the alloy, owing to easier hydrolysis of tantalates. The greater part of it remains in the filtrate after precipitation by phenylarsonic acid.

The little quantities of tantalum and niobium that pass with zirconium into the solution to be colorimetrated render the use of complexone unnecessary.

The above method of analysis was used for determination of zirconium contents in ores.

2. DETERMINATION OF ZIRCONIUM AND HAFNIUM IN MIXTURE BY MEANS OF DISTRIBUTIVE PAPER CHROMATOGRAPHY

Except physical methods of analysis (chiefly spectral and roentgenospectral), the determination of hafnium in mixtures with zirconium may be effected only by indirect chemical methods, based on differences of their atomic weights. We cannot pay much attention to the earlier works. We only note that recently it was suggested that the ratio of *p*-bromomandelates weight to that of the oxides obtained from them should be taken into consideration.[9]

It was necessary to work out a method for direct determination of Hf mixed with Zr, after it is separated, for application of indirect methods brings always a number of obstacles and especially when foreign elements are present.

The properties of Zr and Hf having much in common, chemical methods for their separation are not efficient at one operation. It could be achieved only by means of many repeating operations. Chromatographic methods at which repeating process of separation is automatic are, therefore, the best for this purpose. Chromatography on ion-exchange resins or on silica gel made it possible to obtain more complete separation of zirconium from hafnium.

For analytical purposes, especially wide use has been made of the method of distributive chromatography on paper. The value of this method and its adequacy for identifying various substances of organic and inorganic origin in mixtures has been demonstrated lately in a multitude of cases. Therefore, we tried to apply this method for the separation of zirconium and hafnium and their subsequent determination.

The first problem was to select the conditions required for the separation of the above elements on filter paper. To examine the distribution of zirconium and hafnium on the chromatogram obtained on a strip of paper, the solvent was removed by drying and the chromatogram was developed by moistening with a solution of the "arsenazo" reagent. The position of zirconium and hafnium was determined by the situation of the violet-coloured spots.

As both elements similarly react with the reagent, in order to ascertain the position of the hafnium area, 1–3 microcuries of the radioactive isotope of hafnium-181 were added into a mixture of the salts intended for their separation. The developed chromatogram was cut into pieces and the activity of each piece was measured with a counter, which gave us data on the distribution of hafnium on the chromatogram.

The experiments were conducted with the usual equipment by using both the descending and ascending methods.

Systems of various organic solvents (alcohols, ethers, ketones) and inorganic acids—hydrochloric, nitric and hydrobromic—taken in a concentration of up to 10 per cent to total volume were thoroughly studied. However, in this way no separation could be obtained, in processing with "arsenazo" an unbroken coloured band appeared on a strip of paper, which testifies that the elements moved along the paper not in separate zones but in a whole stream.

Separation was achieved by means of solvents

Table IV. Distribution of Niobium and Tantalum in the Course of Analysis for Determining Zirconium

No.	Weighed ore samples, mg	Contents in ore, %			Distribution of element in course of analysis, %			
		ZrO_2	Nb_2O_5	Ta_2O_5	Filtrate after alkaline fusion	Filtrate after precipitation with phenylarsonic acid	Filtrate after decomp. of phenylarsonate by ammonia	Final hydrochloric acid solution
					(a) Distribution of niobium			
1	500	0.04	0.3	traces	54.5	43.2	0	2.4
2	500	0.2	0.3	traces	67	30.6	2.4	0
3	100	2.0	0.04	traces	11.8	67	6.6	14.6
4	100	2.0	2.54	traces	5.4	83.5	3.35	7.0
					(b) Distribution of tantalum			
5	500	0.04	0.3	traces	0	99.5	0.5	0
6	100	2.0	0.04	traces	0	98.75	0	1.25
7	100	2.0	0.04	2.5	0	99.1	0	0.96

Table V. Distribution of Zones of Zirconium and Hafnium and Distribution of Radioactive Isotope of Hafnium-181 during Chromatography on Paper*

No.	Solvent	Contents of HfO_2 in mixtures, per cent	Range of element areas from the plate of application of the drop of the solution, cm		Content of isotope of hafnium-181 (%) to its total amount, in separate parts of chromatogram			
			Zirconium	Hafnium	In the place of the application of the drop	In the area of zirconium	In the area of hafnium	Between the zones of Zr and Hf
1.	Buthanole HNO_3 55:45	1.0	7.4–12.6	1.6– 4.6	3.7	1.3	95	–
2.	Buthanole HNO_3 1:1	1.0	9.2–15.0	3.6– 7.0	0	5.5	94.5	–
3.	Amylic alcohol HNO_3 7:3	1.0	4.6–10.8	0.8– 3.6	8	0	87	5
4.	Amylic alcohol HNO_3 6:4	1.0	4.8–11.4	1.5– 4.0	6	0	88	6
5.	Ether HCNS	1.0	3.0 20.8	22.6–27.2	0	3	97	–
6.	Ether HCNS	1.0	0.5–12.8	14.2–16.5	0	8.5	91.5	–

* Area of solvent displacement at all tests equals approximately 50 cm.

(butanol and amyl alcohol) containing nitric acid in concentrations up to 30–50 per cent of the volume, as well as by the use of an ethereal solution of thiocyanic acid (2.8–3.0*M*). The latter solvent has been recommended for use in separating zirconium and hafnium by the extraction method.[12]

The position of the areas obtained at the separation of zirconium and hafnium with these solvents and the distribution of hafnium in zones according to its activity are presented in Table V.

When separating with a mixture of solvents with nitric acid, the zirconium zone appears in front (in the direction of the movement of the solvent), while the zone of hafnium is situated behind, nearer to the place where the drop was applied. It is better to make use of amyl alcohol, as in experiments with butanol a certain amount of hafnium remains with the zirconium. With the use of the ether containing thiocyanic acid, the position of the zones is reversed, the hafnium zone being situated in front of the zirconium zone. The zone of zirconium is stretched out along the chromatogram, beginning with the spot where the drop was applied.

The separation proceeds worse than with amyl alcohol and nitric acid, and a certain amount of hafnium remains in the zone of zirconium. The contents of hafnium in one zone calculated from its activity constituted 72% to 93%. The incomplete extraction of hafnium is apparently connected with insufficient washing of the paper for removal of admixtures. The quality of the paper is also of great importance for the successful separation. Sheets of ashless paper employed for preparing filters for quantitative analysis are the best material.

It should be noted that later on after the completion of this work, the papers described the separation of Zr and Hf on filter paper using dichlorethylenetriglycole.[11] However, the quantitative method of analysis was not developed.

To use our method for separating these elements in analysis it was necessary to find some way of determining these elements in the areas after chromatography. Owing to the small quantity of separating elements 100–200 μg it appeared that colorimetry was the most suitable method.

To develop methods for determining the elements in the zones, we applied "arsenazo" and phenylfluorone reagents. The latter is more sensitive and is therefore suitable for determining the elements when their contents in the areas is not large. Colorimetry with phenylfluorone was conducted in 0.5*N* solutions of hydrochloric acid in the presence of gelatine as a protective colloid, with the addition of 0.8 ml of 0.5% of alcohol solution of the reagent to 10 ml of the total volume of the solution after standing it for 1.5 hr. The proportionality of the colour to the contents of elements is observed when zirconium contents is up to 10 and hafnium up to 15 μg, respectively.

It was found convenient to transfer zirconium or hafnium into the solution by burning the paper moistened with a calcium nitrate solution (200 mg/ml CaO) at 700–800° and dissolving the ash in acid (0.5 ml 5*N*). The calcium oxide produced by calcination promotes the dissolution of ZrO_2 or HfO_2 in acid, apparently, due to the formation of calcium zirconate.

The experiments connected with the determination of zirconium (hafnium), spread over paper, showed that in this way these elements may be determined with a satisfactory degree of precision.

The described analytic procedure was applied to the analysis of a mixture of zirconium and hafnium oxides. The oxide was converted to nitrate (or oxychloride as in the case of separation by thiocyanic acid in ether). A drop of the obtained solution was put on paper and "arsenazo" was used to locate the zones. The strips of paper containing the zones of the elements were analysed by the above described method. The results are given in Table VI. After

chromatography with amyl alcohol was completed, the remaining 6–8% of hafnium was determined additionally at the place where the drop had been placed (see Exp. No. 3 and 4, Table V).

The table shows that the results of chromatography coincide within 1–3 per cent with the data of spectral analysis. Taking into consideration some possible error at spectral determination, the coincidence of results may be considered as satisfactory.

The obtained coincidence of results, in spite of incomplete extraction of hafnium by paper chromatography, is evidently explained by mutual compensation of errors due to the presence of a quantity of hafnium in the area of zirconium and vice versa.

3. CONCENTRATION OF HAFNIUM CONTAINED IN PREPARATIONS OF ZIRCONIUM FOR THE PURPOSE OF ITS SPECTRAL ESTIMATION

The determination of little quantities of hafnium in preparations of zirconium during tests of the latter's purity, is usually performed by the spectral method described in literature. At small concentrations of hafnium present in the zirconium preparations preliminarily purified for this purpose, in order to increase the precision and sensitivity of analysis, it is desirable to have a method which could insure preliminary concentration of Hf.

Therefore it was necessary to develop a suitable method of concentration. The use of the paper distribution chromatography was in this case excluded, for the quantities dealt with at separation are very small (0.1 mg) so that it was impossible to get the concentrated product in amounts sufficient for analysis. In this case, the best method for hafnium concentration is that of extraction.

The advantage of these methods is the possibility to obtain quickly the concentrate by simple extraction of substance with organic solvents.

The papers describe methods for separating zirconium and hafnium, based on the extraction of thiocyanates by ether[10] or of compounds with β-diketones, trifluoroacetylacetone[12] and thenoyltrifluoroacetone[1] by benzol. We chose the method of extraction of thiocyanates by ether as it is more accessible and does not require complicated reagents.

Hafnium thiocyanate extraction from solutions of zirconium sulphate did not bring complete separation of hafnium. A considerable part of it remained with zirconium. Therefore we adopted the method of isolation of hafnium concentrates by the ether-thiocyanate extraction from solutions of zirconium oxychloride. Due to the low concentration of hafnium at single extraction, we resorted to the method of countercurrent extraction.

The elements were separated by semiautomatic simplified apparatus with 9–10 funnels fixed to a vertical bar. With the help of a motor the bar was brought into rotatory oscillating movement, so that the funnels oscillate in an horizontal plane.

The procedure consisted of the following:

An immobile phase was placed into each funnel. This phase was an ether solution of thiocyanic acid (2.8–3 *M*) in a quantity of 10 ml. This solution was prepared by shaking up ether with a solution of ammonium thiocyanate, acidified with sulphuric acid. The ether solution was previously brought into equi-

Table VI. Determination of Hafnium Oxide Content in a Mixture of $ZrO_2 + HfO_2$ by the Developed Method

No. of sample	Found in areas, Micrograms ZrO_2	HfO_2	HfO_2 %	Found by the spectral method HfO_2 %	Difference HfO_2 %	Note
1	50	3	5.7	5.0	+0.7	Chromatography with amylic acid, colorimetry with "arsenazo"
2	100	6	5.7	5.0	+0.7	
3	97.5	5	4.9	5.0	−0.1	
4	55.0	6	9.8	10.0	−0.2	
5	194	75	27.8	29.2	+1.4	
6	35	26	40.9	40.0	+0.9	
7	25	40	61.9	60.0	−1.9	
8	35	80	69.5	68.0	+1.5	
9	54	4	6.9	5.0	+1.9	Colorimetry with phenylfluorone
10	30	13	30.1	30.0	+0.1	
11	10	19	65.5	68.0	−2.5	
12	6	11	65.0	68.0	−3.0	
13	2	48	96.0	92.0	+4.0	
14	98	13	11.8	10	+1.8	Chromatography with ether with hydrothyocyanic acid, colorimetry with "arsenazo"
15	60	21	26.0	29.2	−3.2	
16	37	13	26.0	29.2	−3.2	
17	48	71	59.9	60.0	−0.1	
18	25	50	66.6	68.0	−1.4	With phenylfluorone

Table VII. Tests of Method of Concentrating Hafnium by Means of Countercurrent Extraction

No.	Weight of sample, mg	Content of oxides in fractions (mg): Water fractions 1–4 Wt	Water fractions 1–4 % HfO_2	Water fractions 5–9 Wt	Water fractions 5–9 % HfO_2	Ether fractions 10–13 Wt	Ether fractions 10–13 % HfO_2	Ether fractions 14–15 Wt	Ether fractions 14–15 % HfO_2	Ether fractions 16–18 Wt	Ether fractions 16–18 % HfO_2	Total hafnium found, mg	Total hafnium found, %	Maximum degree of concentration
1	298	43	—	117	—	96	—	28	0.55	14	2.0	0.43	0.14	14
2	288	43	—	118	—	56	—	15.2	0.27	5.5	2.7	0.19	0.08	34
3	274	53.4	—	153	—	53.6	—	10.8	0.2	3.0	2.2	0.09	0.03	73
4	315	14	—	195	—	76	—	20.0	0.45	10	1.95	0.29	0.09	21
5	217	31	—	90	—	72	—	16.0	0.45	8	2.2	0.25	0.11	22
6	189	33.8	—	80.4	—	50.9	—	16.4	traces	7.4	1.35	0.1	0.05	27
7	284	67	—	158	—	42	—	12.0	0.39	5	0.98	0.1	0.035	28
8	267	32	—	110	—	93	—	22	traces	10	0.86	0.09	0.034	25

librium with the mobile water phase, which consisted of various ammonium salts acidified with acids. Zirconium oxychloride, containing various amounts of hafnium, was dissolved in a definite quantity of water solution of cyanic acid (5 ml) and the obtained solution was successfully shaken up and brought into equilibrium with each of the ether solutions contained in the funnels. After that, 9–10 portions of water salts solutions, which were collected, separately, were brought into the state of equilibrium with each of the other solutions. The time of shaking for obtaining equilibrium was 2 minutes. As a result of separation, 18–20 portions of the solution were obtained the number of water and ether solutions being 9–10 respectively. The summary content of zirconium and hafnium oxides in each fraction was determined by weighing; the distribution of hafnium between phases is determined by measuring the distribution of the radioactive isotope of hafnium-181 and besides through spectrographical analysis of the extracted sum of oxides.

The results of the studying of zirconium and hafnium separation by means of countercurrent extraction may be presented as follows:

1. If a mobile water phase is a solution of cyanic acid without any addition of salts, hafnium is distributed into fractions. In this case, the distribution coefficient of hafnium is 2.5–4.0; that of zirconium 0.3–0.5.

Due to this, hafnium is concentrated in the ether fractions while zirconium in those of water. Complete separation of the elements by apparatus with 10 funnels is not achieved. A certain amount of hafnium remains in an unextractable form. In the case of oxychloride, this amount comprises 4.2–4.5% from the total amount; in the case of perchlorate, 1.4%. The other 95.5–98.6% of hafnium are extracted apparently in the form of specific compound having its own definite distribution coefficient.

2. The addition of ammonium chloride to the water phase promotes the reduction of the unextractable amount of hafnium, improving separation. The distribution of hafnium and zirconium in phases, in this case, remains practically the same.

3. Separtion is improved when in addition to ammonium chloride, sulphuric acid is introduced into the water phase in a concentration of 0.3–0.45*M*. Zirconium, in this case, is selectively retained in the water phase, while the passage of hafnium into the ether phase remains the former. The coefficient of zirconium distribution in the phases is approximately 0.25, that of hafnium, 2.5. That is why the ether fractions contain about 90% of the total hafnium. It must be noted that with the further increase of sulphuric acid concentration in the water phase to 0.6 *M*, the quantity of unextractable hafnium retained in the first water fractions increases as well. One can isolate 97.5% of the total hafnium by twenty-six fold concentration, provided the two remaining water fractions are added to the ether fractions.

On the basis of the conducted experiments, the following method was chosen for the concentration of hafnium from zirconium preparations before spectral analysis. The zirconium preparation to be analysed (zirconium oxychloride) is dissolved in 10% ammonium chloride solution brought into equilibrium with an ether solution of thiocyanic acid, and is subjected to separation by the method of countercurrent extraction.

From the combined fractions of the ether solutions zirconium oxide is extracted and subjected to spectral analysis.

To test the possibility of concentrating hafnium by this method, a number of zirconium oxide samples containing various portions of hafnium was, after conversion into oxychloride, subjected to separation by the described method; the obtained water and ether solutions were mixed in groups of 3 or 4 and poured together; oxide was extracted from the combined solutions by means of evaporation and precipitation with ammonia. The oxide was analysed by spectrographic method. The separation was effected in 9–10 funnels, with no addition of sulphuric acid to the water solutions.

The results of the work are presented in Table VII.

As it is seen from the table, hafnium could be detected spectrographically only in the last fractions, 14–18. The maximum degree of enrichment averages 30. Thus, when combining fractions by 2 or 3 when the enrichment is effected, the sensitivity of spectral analysis for Hf increases 30 fold (see Table VII). It must be noted that the hafnium content determined in this way is somewhat lower than the actual, due to its incomplete passage into the ether fractions, and must be increased by 10%.

CONCLUSION

The use of the radioactive isotope of hafnium-181 proved effective in developing analytic methods of determining the content of zirconium and hafnium. It made it possible to observe the distribution of elements during analysis, and find possible losses and value of errors. As a result of these investigations the following methods were developed:

1. A method of colorimetric determination of zirconium in ores with preliminary concentration of the zirconium by precipitation with phenylarsonic acid makes it possible to determine zirconium in ores with zirconium content 0.005–0.2%, with an error 5–10% (relative).

2. A method of colorimetrical analysis of zirconium-hafnium mixtures with the use of paper chromatographic separation. This method allows to determine hafnium in mixtures with zirconium; hafnium content being 5–95%, with possible errors from 1 to 3%.

3. A method of concentrating hafnium from zirconium preparations by means of countercurrent extraction for purposes of spectral analysis, by means of which the concentration of hafnium in samples is raised 30-fold.

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Record of Proceedings of Session 17B.1

WEDNESDAY MORNING, 17 AUGUST 1955

Chairman: **Mr. C. Eichner (France)**

Vice-Chairman: **Mr. R. Henych (Czechoslovakia)**

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Programme

P/533	Zirconium metal production	S. M. Shelton
P/347	Separation of zirconium from hafnium	J. Huré and R. Saint-James
P/876	Separation of hafnium from zirconium by vapour phase dechlorination	B. Prakash and C. V. Sundaram

DISCUSSION

Mr. S. M. SHELTON (USA) presented paper P/533 as follows:

Zirconium is a new metal. Although discovered by Klaproth in 1789, it was made in ductile form first in 1925 by van Arkel, de Boer and Fast, in the Netherlands. The de Boer process, commercialized by Phillips in the Netherlands and by the Foote Mineral Company in the United States, is an ingenious scheme of thermal decomposition of zirconium tetraiodide on a hot filament, forming high-purity ductile metal as a rod, usually of large crystals. Von Zeppelin in Germany made ductile zirconium in 1940, by reducing, with magnesium, zirconium tetrachloride dissolved in fused sodium chloride.

In 1945 Kroll, who had moved from Luxembourg to the United States, initiated at the Bureau of Mines a development program for zirconium analogous to his titanium process, using magnesium to reduce zirconium tetrachloride in an inert atmosphere furnace, under controlled temperature, pressure and rate of reaction.

Recently Horizons, Inc., in the United States has reported the experimental production of ductile zirconium by electrolysis of fused mixed fluorides in the temperature range 800°C to 850°C.

Zirconium has many interesting physical and mechanical properties. It competes with tantalum in resistance to corrosion in acids and corrosive salts. But because of transparency to thermal neutrons and resistance to corrosion in hot water and liquid sodium, it has found its greatest use as a construction material in nuclear reactors. In fact, this field of use has dominated the output of high-purity zirconium in the United States almost completely, leaving little or no metal for other purposes.

Miller of England has stated: "The properties of zirconium make it particularly useful in thermal reactors, especially if they are to be used for power production, where neutron economy and regeneration of fuel are important. In addition to a low neutron absorption cross section, other stringent demands are placed on structural materials and components in power reactor systems. They include (1) mechanical strength and stability under the severe stresses resulting from high thermal gradients, (2) leak-tight reliability in high temperature, high pressure, corrosive, dynamic, and radioactive cooling systems, (3) resistance to mechanical damage by radiation, (4) limited formation of high-activity products by nuclear reactions, and (5) adaptability to simple remote maintenance and repair."

Zirconium apparently meets these requirements.

At the instigation of the Atomic Energy Commission, the Albany Laboratory of the Bureau of Mines expanded Kroll's development pilot plant to a production scale. Additional operating steps were added to complete the flow sheet shown in Slide 1 (Fig. 20 of P/533).

The reduction of hafnium tetrachloride to metallic sponge follows the same procedure, on a smaller scale, as the reduction of zirconium tetrachloride to metallic sponge. However, the hafnium metal sponge is not sufficiently pure to be ductile. It must be refined by the de Boer or iodine process before melting to ingots.

Returning to the flow-sheet, the purification step was designed primarily to separate hafnium from zirconium by liquid-liquid solvent extraction.

Commercial-grade zirconium tetrachloride, containing 2 to 3 per cent hafnium with respect to zirconium, was solubilized in hydrochloric acid solution and ammonium thiocyanate was added. The solution was filtered and fed through a storage tank to the plant as shown in slide 2 (Fig. 21 of P/533). The extraction system was made up of four glass columns. The feed solution entered at the top of the first column and passed countercurrent to methyl isobutylketone solvent containing thiocyanate which entered the bottom of the system. The aqueous solution or raffinate leaving the system was low in hafnium. It was passed to the fifth column countercurrent to fresh solvent containing no thiocyanate. The

raffinate stripped of thiocyanate was filtered and pumped to storage tanks. The solvent was mixed with cleaned solvent and pumped to the bottom of the extraction system. The solvent from the extraction system contained hafnium and a relatively large percentage of zirconium. On leaving the extraction system it entered the bottom of the first of three stripper columns and passed countercurrent to hydrochloric acid solution which stripped zirconium, slightly contaminated with hafnium, from the solvent and returned it to the feed pump.

Scrubbing or solvent cleaning was accomplished by passing the solvent, stripped of zirconium, countercurrent to sulfuric acid solution. Essentially all metallic ions, including cadmium, boron and titanium, were removed with the hafnium from the solvent. The aqueous but impure hafnium sulfate was filtered and pumped to a storage tank. The zirconium-bearing raffinate, after being tested, was treated with either di-ammonium phthalate or sulfuric acid to precipitate the zirconium. Phthalate was used first and the change was made to sulfuric acid during the last months of operations because of lower cost and higher efficiency.

The filter cake was washed with dilute ammonium hydroxide solution, dried and calcined to zirconium oxide.

Slide 3 (Fig. 22 of P/533) is a photograph of the base of the glass extraction columns. It should be noted that they were open columns and not pulse columns.

The major difficulty in handling both hydrochloric acid solution and a solvent in the same system was corrosion. Rubber was attacked by the solvent. Glass and zirconium metal withstood corrosion most satisfactorily.

To prepare a feed material for the reduction furnaces it was necessary to convert the calcined zirconium oxide to zirconium tetrachloride.

The zirconium oxide was blended with high-purity carbon powder and a binder. The mixture was briquetted in a Belgian roll-type briquetting machine and the briquets, about walnut size, were fed to chlorination furnaces diagrammed in Slide 4 (Fig. 28 of P/533).

The bed of briquets in the furnace at 600°C to 800°C furnished electrical resistance to voltage from three graphite electrodes in the furnace wall. Chlorine gas was fed in the bottom of the furnace. The reaction product was zirconium tetrachloride gas which was condensed as light crystals in the two condensers. Glass scrubbing towers cleaned the effluent gas which was discharged to the atmosphere. Zirconium tetrachloride was tapped at intervals from the bottom of the first condenser directly into drums of sufficient size to constitute one batch for the reduction furnaces.

Slide 5 (Fig. 32 of P/533) is an interior view of the reduction plant. The battery of furnaces of identical size on the lower floor was for reduction of zirconium tetrachloride to zirconium metal sponge. The battery of furnaces, also of identical size, on the mezzanine was for melting and distilling, under vacuum, the magnesium chloride and excess magnesium from the batch of zirconium sponge.

Slide 6 (Fig. 33 of P/533) is a diagramatic view of the reduction furnaces. Raw zirconium tetrachloride was contained within the furnace in a open-top drum. Beneath the drum was a crucible which initially contained magnesium metal. The top of the furnace was sealed in place with lead-antimony eutectic alloy. A cooling coil was attached to the furnace top within the furnace atmosphere.

The furnace operation was to heat the zirconium tetrachloride at temperatures below its sublimation temperature for several hours to evolve and drive off volatile impurities through the bleeding valve. When the tetrachloride had been degassed, the furnace was back-filled with helium and the lower zone containing magnesium metal was heated to its melting point. The lead antimony seal was melted and the zirconium tetrachloride heated to its sublimation temperature.

A too-rapid reaction rate would result in overheating and alloying the iron crucible with zirconium. Low temperatures slowed down the reaction and Iron and zirconium form a eutectic at about 930°C. reduced capacity. The liquid-lead seal acted as a safety valve to maintain furnace pressure at less than about 2 psi above atmospheric pressure. The cooling coil was a thermal baffle to help control the furnace atmospheric temperature and rate of sublimation. The zirconium tetrachloride gas passed over the top of the drum container and down through the baffles to come in contact with liquid magnesium metal. It was important that the arrangement prevented non-volatile impurities in zirconium tetrachloride from coming in contact with magnesium. When the reaction was completed, the crucible was essentially full of magnesium chloride containing zirconium sponge beneath the surface. The furnace was cooled and the crucible, containing solid magnesium chloride in which zirconium sponge was submerged, was removed for treatment in the distillation furnaces.

Slide 7 (Fig. 37 of P/533) is a diagram of the hot-top bell-type distillation furnaces. The crucible was turned upside down and raised from the bottom into the furnace. The salt can and baffles were inserted. Then the furnace was sealed, heated and evacuated. There were two vacuum system, one between the bell-type furnace and the retort which protected the hot retort against collapse against atmospheric pressure, the other within the retort itself. As the furnace was heated, magnesium chloride melted in the hot upper zone and drained down to the salt cup in the cool lower zone. Continued heating under vacuum sublimed the residual magnesium chloride and magnesium metal from the zirconium metal sponge in the crucible. The sublimation products condensed in the lower cold zone. When the

operation was complete, the furnace was partially cooled to a safe temperature and the bell furnace was lifted from the retort. This permitted the retort to be cooled by water spray at a rapid rate. The retort was filled with helium and cooled almost to room temperature. Then the zirconium sponge was conditioned by admitting dry air to the retort before the crucible containing the sponge was removed from the retort.

Slide 8 (Fig. 41 of P/533) sketches a cross section of a typical batch of zirconium sponge in the crucible after distillation. During reduction presumably the *B* and *E* zones deposited first. *E*, a thin surface plate on the crucible wall, was returned for chlorination. *B* apparently acted as a getter. It was relatively high in metallic impurities. *A* sponge was less compact but low in both metallic impurities and in volatile impurities. *C* sponge, the last portion to form during reduction, contained the lowest percentage of metallic impurities, but also contained volatiles which were troublesome in melting. Each zone was separated visually, cleaned, crushed to — ⅜ in. mesh and analysed. On the basis of weights and analyses, a batch of 2000 pounds of uniform analysis was selected by calculation and carefully mixed in a mechanical blender. A typical analysis of an acceptable blended bath of 2000 pounds showed less than 150 parts per million of nitrogen, less than 4000 parts per million of iron, less than 200 parts of silicon, and less than 100 parts per million of aluminum. Oxygen was in the range of 800 to 1000 parts per million.

The blended batches of crushed zirconium were made ready for treatment for melting. The sponge was cold compacted under high pressure into bars of square cross section 2 in. × 2 in. and 20 in. long. The most successful melting procedure was to double-melt the zirconium and zirconium alloys in cold-crucible, consumable arc furnaces, in a helium atmosphere and under vacuum.

Slide 9 (Fig. 64 of P/533) outlines the furnace for melting the cold compacted zirconium sponge. Compacted bars were stored in the upper chamber. The system was evacuated and back-filled with helium to atmospheric pressure. By using rubber gloves attached to the chamber wall, the compacted bars were manually butt-welded and lowered through the contact section to the crucible. Provision was made for adding alloying agents, as pellets, fed at a controlled rate to the crucible. The arc was struck by lowering the welded bar to contact zirconium in the bottom of the crucible, made of copper and jacketed in water which flowed at a high velocity. The heat of the arc melted the compacted zirconium into a pool of liquid metal, which spread out to fill the crucible. As the compacted metal was being melted, additional bars were butt-welded to the top of the bar, which gradually descended to the crucible. The completed ingot was 7 inches in diameter and about 24-inches long.

Four of the 7-inch ingots were attached end to end with stud bolts of zirconium and by welding to make a complete electrode for remelting.

Slide 10 (Fig 66 of P/533) shows the remelting furnace. This furnace was operated under partial vacuum. The fabricated electrode attached to a copper busbar was gradually lowered into an electric arc which melted the electrode into an ingot 10 inches in diameter. A water-cooled copper crucible was used in the same manner as in the first melt.

On both furnaces, an induction coil of direct current round the crucible tended to control the arc vertically and to prevent it jumping to the crucible wall. The ingots were finally conditioned in a lathe by removing 1/16 inch to ¼ inch of rough surface which sometimes contained small gas pockets and bubbles.

It is of interest that these furnaces became the prototype for furnaces melting titanium and thorium successfully with essentially no contamination during melting. The plant was closed down in May 1955. The Carborundum Metal Company in the United States is now meeting requirements for zirconium.

Mr. J. Huré (France) presented paper P/347.

Mr. B. Prakash (India) presented paper P/876.

DISCUSSION OF P/533, P/347 and P/876

Mr. G. A. Meyerson (USSR): The papers by Mr. Shelton, Mr. Huré, and Mr. Prakash have described interesting research on new methods of separation of hafnium from zirconium.

It is, however, still profitable to use the older method of fractional crystallization of potassium fluozirconate, provided that it is used in conjunction with a method of decomposing the zirconiferous ore that will produce potassium fluozirconate immediately in the first stage of the process.

Research on the development of a combined technique of this kind is described in the Soviet paper P/634 by Sajin and Pepelyaeva.

The zirconium ore concentrate is sintered with potassium silicofluoride at 650–700°C, yielding potassium fluozirconate, which is then leached with hot dilute acid.

When the solution has cooled, crystals of potassium fluozirconate are precipitated; these are then treated by fractional crystallization. To increase the crystal yield, the salt to be recrystallized is dissolved not in pure water but in the mother-liquor from the previous crystallization.

Under these conditions, 16–18 crystallizations are enough to reduce the hafnium content from 2.5 per cent in the starting product to less than 0.01 per cent in the end-product (calculated as a percentage of the zirconium).

In view of the fact that the immediate product of the decomposition of the concentrate is recrystallized, that the separation of the fluozirconate from hafnium by this method does not require reagents of any kind, and, further, that the yield of zirconium

in the final crystal fraction is about 80 per cent, the technique described can be regarded as quite simple, efficient and economical.

Mr. A. R. KAUFMANN (USA): I should like to ask Mr. Prakash whether he feels that his method can be used to get the hafnium content down to something like 0.01 per cent.

Mr. PRAKASH (India): After three de-chlorination treatments, zirconia was obtained which contained 0.3 per cent hafnium. A freak value of 0.05 per cent hafnium was once obtained after a single treatment, but this value was not reproducible in later tests. It may be that segregation in the charge of gases and vapour takes place in the reaction chamber and promotes the formation of hafnium oxide in regions low in chlorine gas. Once formed, it will be difficult to re-chlorinate the hafnium oxide under the conditions prevailing in the reaction chamber. If this analysis is correct, improvements in technique in order to prevent segregation should result in giving low hafnium in zirconia by a single treatment. Such tests are under progress and will be reported in literature when data become available.

Mr. SHELTON (USA): I have a comment on the papers presented by Mr. Huré and Mr. Prakash. Their approaches are different from ours. They are very interesting. The problem in itself in separating hafnium from zirconium is not so much the efficiency of the separation, because we feel that we can do that, but the cost. Inherently these processes of separation are costly. The paper presented by Mr. Prakash is particularly interesting in that it seeks to get low hafnium in zirconium, and in all probability it could be done at a much lower cost than by the other two methods.

Mr. M. BENEDICT (USA): I should like to ask Mr. Prakash whether the thermodynamic data which he cited have been confirmed experimentally, by, for example, measurements for the ratio of chlorine to oxygen over mixtures of the chloride and oxide of these two elements, or whether the values are simply calculated.

Mr. PRAKASH (India): These are calculated values from the free energy data.

Mr. BENEDICT (USA): They would be interesting.

Mr. PRAKASH (India): Yes, that would be an interesting approach. It may turn out that the difference in equilibrium $P_{Cl_2} : P_{O_2}$ ratios for the two reactions is not as wide as is indicated by thermodynamic data.

Mr. A. A. SMALES (UK): Mr. Shelton mentioned a nitrogen figure in his zirconium sponge of less than 150 ppm. Can he say whether this figure was obtained by a chemical method or by a vacuum diffusion method, and has he any view on the relative merits of these and any other methods as applied to the determination of nitrogen in zirconium?

Mr. SHELTON (USA): The nitrogen determinations were made chemically by the Kjeldahl method. We have thorough confidence in that method of analysis, and the results are readily reproducible. We have never attempted any spectrographic analysis of nitrogen in zirconium.

The CHAIRMAN: I should like to put two questions to Mr. Shelton. You have stated that a pilot plant in Albany has not been working since May 1955. Is the complete process now used by the Carbide and Carbon Chemical Corporation? Does the Carbide and Carbon Corporation also use the zirconium process as you have described it?

My second question is this: Could you tell us something about the possibility of improving the resistance of zirconium by the study of new alloys?

Mr. SHELTON (USA): Zirconium is now being produced by the Carborundum Metals Corporation, presumably at a rate to meet the requirements of the United States, and I think they have metal for sale commercially. The question of alloys can be dealt with by saying that in terms of corrosion resistance undoubtedly certain of the alloys are superior to pure zirconium for different types of corrosion resistance, but that field has not been explored sufficiently to give any definite data.

Session 17B.2

PRODUCTION TECHNOLOGY OF SPECIAL MATERIALS: BERYLLIUM

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Technology of Manufacturing Items of Pure Beryllium and Beryllium Oxide for Use in Nuclear Reactors*

By G. A. Meyerson, USSR

In producing atomic energy for peaceful purposes metallic beryllium and its oxide are used as neutron moderators.

BERYLLIUM OXIDE AND SOLID BODIES MADE OF IT

Technical beryllium oxide is obtained from beryl concentrates by well-known chemical methods.

Methods have been developed for the production of high-purity beryllium oxide suitable for use in nuclear reactors. The purest beryllium oxide is obtained by treating technical beryllium hydroxide with glacial acetic acid, the product of this reaction being the volatile basic acetate $BeO \cdot Be_3(CH_3COO)_6$ which is separated from all impurities by distillation.

This reaction has been known for a long time in analytical chemistry; it has been used also for the production of beryllium compounds of the highest grade of purity for laboratory studies of their properties.

In the USSR an industrial method has been developed for the production of highest grade beryllium oxide, base on the distillation of the basic acetate. Freshly precipitated technically pure beryllium hydroxide is treated with acetic acid. The basic beryllium acetate is distilled in continuous-flow type apparatus at 360–400°C. After two distillations the basic acetate, freed from impurities, is decomposed at 600–700°C, to form the oxide as a highly dispersed powder.

The quantities of impurities contained in the original material and in the purified product in relation to the beryllium content in these products are given in Table I.

This oxide corresponds to the purity requirements for articles to be used in nuclear reactors.

The requirements for beryllium oxide bodies differ according to the conditions under which they are to be employed. For this reason, a number of methods of preparing such bodies have been developed, from those very simple ones to those requiring complicated apparatus and precision technology.

The simplest method of producing sound bodies from beryllium oxide is by packing it into graphite dies and firing them at 1800°C. If the article is hollow (crucibles, tubes), the cavity is filled with disintegrated graphite. The dies are packed with a mixture of different batches of beryllium oxide calcined at various temperatures (fine-grained at 1200°C and coarse-grained at 1800°C). After firing the articles have a density of 2.1–2.2 gm/cm³.

Another method has been developed for the production of bodies with higher densities, consisting in the hot pressing of the beryllium oxide in graphite dies under a pressure of 18–20 kg/cm² and at a temperature of about 1800°C. The density of bodies made in this way is up to 2.75 gm/cm³.

Still denser (2.9 gm/cm³) and degassed bodies are produced by hot pressing the oxide under vacuum, bodies produced by this method having densities close to the theoretical one. As a result of the evaporation of impurities at high temperature and under the vacuum used in this method, the bodies are purer than the initial beryllium oxide; their mechanical properties are several times higher than those of bodies prepared by ordinary ceramic technology. The method of hot pressing under vacuum which has been developed consists in packing the beryllium oxide powder into dies and briquetting them under vacuum (10^{-4} mm Hg) at a temperature of 1850–1900°C and a pressure of 15–20 kg/cm².

The production of high-purity beryllium oxide and sound bodies from it is controlled by neutron analysis methods developed for this purpose. The behaviour of a number of impurities has been studied using radioactive isotopes (radioactive yttrium, europium, chromium, cobalt, etc.).

PRODUCTION OF HIGH-PURITY BERYLLIUM AND SOUND BODIES MADE OF IT.

High purity metallic beryllium is produced from the technical hydroxide, the composition of which has been given above.

One of the methods of producing the pure metal is by electrolysis of a mixture of fused beryllium and sodium chlorides, taken in a ratio of 1:1 by weight at a low temperature (320–350°C). Conditions of chlorination and electrolysis have been developed which make it possible to remove a number of impurities and hence to set less rigid requirements as to the purity of the initial hydroxide. A furnace has been designed for chlorination and a condenser for recovering the beryllium chloride, permitting a chloride of satisfactory grade to be ob-

Original language: Russian.

* The paper is prepared on the basis of the materials available at the Academy of Sciences of the USSR and the Ministries.

Table I. Impurities in Original Beryllium Hydroxide and in Purified Oxide

Impurity	*Impurity content, per cent of beryllium content*	
	Initial technical beryllium hydroxide	*Purified beryllium oxide*
Iron	0.030–0.100	0.001–0.003
Aluminium	0.500–1.500	0.003–0.007
Silicon	0.100–0.500	0.010–0.020
Manganese	0.010–0.015	less than 0.0003
Copper	0.010–0.015	less than 0.0005
Nickel	0.003–0.005	less than 0.002
Boron	10^{-4}	10^{-5}

tained under properly selected conditions without secondary distillation.

The technical beryllium hydroxide is calcined, and the oxide thus obtained is briquetted and chlorinated at 550–650°C in continuous-flow furnaces lined with quartz and having internal heater.

The sublimed beryllium chloride is condensed at 250–280°C in air-heated nickel condensers with discharge hatches through which the product is drawn off intermittently into removable nickel containers which are fastened hermetically to the hatches.

An electrolyser with detachable nickel electrodes has been designed, allowing the electrolysis to be carried out in two stages. During the first stage, at low voltages (about 1.5 v) metals more positive than beryllium are deposited, after which the electrode is replaced, and high-purity beryllium is deposited on the new electrode. Unlike the methods described in literature, the electrolysis in this case is semi-continuous the process being interrupted for very short periods to replace the cathode and correct the composition of the bath.

In the course of one cycle of electrolysis the beryllium content in the electrolyte decreases from 6.3% to 5.9%, i.e., remains almost constant. A study of the dependence of the viscosity of the electrolyte on the temperature showed that the temperature of the bath should be raised to 370–380°C before replacing the cathode; this ensures the necessary fluidity of the electrolyte, and its maximum return to the bath when the cathode is lifted out.

The electrode with the deposited metal is washed with water to remove the greater part of the electrolyte, then the beryllium powder is passed over a 2-mm screen, and after a number of additional washings the finest part of the powder, which is higher in the impurities content, is refined.

A method of separating the cathode metal from the chlorides has been developed consisting in direct sublimation of the latter in a vacuum furnace at 650–700°C. The sublimed chlorides and the melted electrolyte are collected in a cooled nickel container, from which they are returned to the electrolyser. This simplifies treatment of wastes and considerably increases the direct yield of beryllium.

Beryllium produced by the electrolysis of fused salts contains crystals of various shapes and sizes.

For those cases where the permissible impurity content in the metallic beryllium is higher, a method of thermal reduction of its fluoride with magnesium has been developed. The technically pure beryllium oxide is dissolved in hydrofluoric acid, to which ammonium fluoride is added to form ammonium fluoroberyllate; the solution is purified to remove admixtures of iron, manganese and some other metals by the sorption method followed by an additional treatment with organic compounds containing sulphur. The ammonium fluoroberyllate is subjected to thermal decomposition in graphite crucibles at 900–1000°C; the ammonium fluoride, which evaporates off, is collected in scrubbers and returned to the process. The fused beryllium fluoride obtained is reduced with distilled magnesium in induction furnaces, in graphite crucibles. Towards the end of the operation the temperature in the furnace is raised to 1300°C. A new reduction charge composition has been developed, in which the excess of beryllium fluoride has been replaced by barium fluoride, increasing the beryllium yield.

The fused beryllium bead rises to the surface of the slag, is extracted from the crucible and freed from the salts sticking to it by washing with water.

The process of purification of the beryllium from slag has been improved: after washing with water the beads are kept under vacuum at a temperature close to the melting point of the metal (about 1100°C). Beryllium produced by electrolysis of the chloride or by reduction of the fluoride is remelted to remove volatile admixtures.

This is done in an argon atmosphere at a pressure of 20 mm Hg and a temperature of 1500–1550°C.

The purest beryllium is obtained by a distillation of the technical metal under vacuum. At a temperature of 1300–1400°C and a residual pressure of 1×10^{-5} mm Hg beryllium evaporates very rapidly (about 0.3 gm per hour per cm^2 of metallic surface). The metal is condensed in a molybdenum reflux condenser set up inside a tube of beryllium oxide which is electrically heated by means of a molybdenum winding.

The impurities are condensed in various temperature zones. The purest beryllium is condensed in the zone having a temperature range of 1120–1150°C; most of the aluminium and manganese condenses in the upper parts of the reflux condenser in the temperature range of 900–1000°C.

Distillation under vacuum yields very pure beryllium. The analysis of the original and distilled beryllium are given in Table II.

The remelted beryllium ingots produced as described above are non-homogeneous and coarse-grained in structure. Castings can be hot extruded, but the material is brittle and the mechanical strength of the articles is not high enough. For this reason powder metallurgy methods are the best for the production of solid bodies from beryllium; these methods give articles with a fine-grained homogeneous structure and high mechanical properties.

Several ways of the powder metallurgy have been developed for the production of solid bodies from

Table II. Impurities in the Original and Distilled Beryllium

Impurity	Impurity content, per cent of beryllium content	
	Original metal	Distilled metal
Iron	0.300	0.005
Aluminium	0.090	0.003
Copper	0.024	0.004
Nickel	0.005	0.003
Chromium	0.020	0.005
Manganese	0.015	0.002

metallic beryllium, each of which is used for articles to be employed under different conditions. One of the chief requirements for beryllium articles intended for use in nuclear reactors is high heat resistance, which depends largely on the density of the metal. A method of hot pressing of the powder under vacuum has been employed to obtain compacts of maximum density, approaching the theoretical value, and at the same time to degas the metal. The hot pressing is carried out in lined graphite-dies induction heated to 1100°C. At this temperature the plasticity of the metal is increased to such an extent that a pressure of 50 kg/cm^2 is quite sufficient to produce a practically non-porous body. The residual thermal stresses due to hot pressing are removed by annealing the bodies under vacuum at 1100°C, followed by slow cooling. This treatment also raises the heat resistance of the beryllium. Articles produced by the method described above are intended for long-term service under high temperature conditions.

A method of hot pressing of beryllium powder or chips in a heat-resistant alloy open die at 600°C and a pressure of 5 tons/cm^2 has been developed for the production of high-density articles to be used at the temperatures lower than those mentioned above. The equipment required is not complicated, but this method also secures bodies with densities close to theoretical (1.84–1.85 gm/cm^3).

Degassed metal bodies of the same density can be obtained by a method of preliminary vacuum sintering of compacts cold pressed from the powder. The subsequent hot coining of the sintered briquettes is carried out in open press-dies of a heat-resistant alloy. The conditions of hot coining are similar to those of hot pressing described above. The last two methods should also be followed by annealing under vacuum at 1100°C and slow cooling; during this operation the hardness of the metal is decreased by 10–15 Brinell units.

Articles intended for service under the lowest temperature can be produced by the simplest powder metallurgy method, which yields bodies of low residual porosity (density 1.76–1.82 gm/cm^3). According to this method, the beryllium powder is briquetted in steel dies at a pressure of up to 15 tons/cm^2. The briquettes are then sintered under vacuum at 1150–1200°C, coined cold at the same pressure, and annealed under vacuum at 1000–1100°C.

A method has been developed for the production of beryllium articles in the shape of rods and tubes by hot extrusion of ingots made by a powder metallurgy method. It has been established experimentally that the optimum extrusion temperature is between 500°C and 600°C. The degree of deformation is 85 per cent. The die has an entrance cone at an angle of 60–90°, which passes gradually into the cylindrical part. The extruded bars have a porosity less than 0.5–1 per cent. The Brinell values of the densest beryllium articles after annealing are 90–115 kg/mm^2. The tensile strength of the annealed articles is 50–70 kg/mm^2, and that of the extruded bars is 65-90 kg/mm^2, depending on the degree of reduction.

In order to raise the heat resistance of beryllium bodies keeping their densities high at the same time, methods of alloying the beryllium with special additions during remelting have been developed, as well as methods of applying protective coatings to the articles. These methods can also be employed to increase the heat resistance of articles with a certain degree of residual porosity. Beryllium bodies treated in this manner can endure several thousand hours exposure to air at high temperatures without appreciable changes.

Status of Beryllium Technology in the USA

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Beryllium has been studied by many people for the last thirty years in an effort to develop commercial uses for the pure metal. Such applications, except for X-ray tube windows, at first did not materialize, largely because the metal as ordinarily produced by casting was too brittle for engineering use. A renewed interest in beryllium arose with the development of nuclear energy. Pilot-plant-scale experimentation aimed at improving the quality of the metal and casting in vacuum was started in the USA in 1941 by the Brush Beryllium Company. In 1943 government financed larger scale methods for vacuum melting,[1,2] casting, and extrusion were developed by personnel at the Massachusetts Institute of Technology and the University of Chicago using mainly Brush crude commercial metal in lump form. Beryllium flake supplied by the Clifton Products Company and pebble metal made by the Beryllium Corporation were also used. By 1945 it was possible to make sound castings weighing up to 50 pounds and to extrude rods and flats.[3,4] At the same time a careful study of the physical metallurgy of beryllium and beryllium-rich alloys was carried out.[3] The net result of this work was to show that fabricated beryllium could have a small amount of ductility at room temperature but that there was little promise of producing truly ductile metal either by further purification or by alloying.

During 1946 to 1950 the Brush Beryllium Company developed methods for making a high quality beryllium powder and for consolidating this into large blocks of high density, fine-grained metal. The Brush material has a small amount of ductility at room temperature and in addition is more uniform in properties such as machinability and corrosion resistance than the cast and extruded metal. For these reasons it has entirely replaced the latter in all applications. Brush is now substantially the sole supplier of pure beryllium metal and fabricated parts for nuclear applications in the United States of America.

The extrusion of Clifton electrolytic flake beryllium and of Brush powder has been practiced by the M.I.T. group (now Nuclear Metals, Inc.) for a number of years. The technique has been advanced to the point where uniform rods and flats can be produced having surprisingly large ductility in the extrusion direction but only 1% to 2% in the transverse direction. This material when cross rolled develops even greater ductility in all directions in the plane of the sheet, but presumably is still brittle perpendicular to the plane.

The ductility of powder metallurgy and of fabricated beryllium is not intimately related to purity. For this reason the production operations at Brush are for practical reasons adjusted to give only the degree of purity deemed desirable for nuclear or corrosion reasons. Beryllium oxide is of interest, also, as a reactor material even though it has not found such use as yet in the United States of America. For these reasons, a brief account of the preparation and properties of beryllium oxide will be given in the following discussion.

A comprehensive book on beryllium has been prepared by various people in the United States of America at the instigation of the United States Atomic Energy Commission and the American Society for Metals and is about to be published. References to this book will be made in this article and interested persons should consult it for greater detail than can be given here.

SOURCE OF BERYLLIUM AND AVAILABILITY OF BERYLLIUM MINERALS

Beryllium is found in about thirty minerals, but occurs principally in beryl ore, a crystalline form of beryllium aluminum silicate of the theoretical formula $3BeO \cdot Al_2O_3 \cdot 6SiO_2$. Commercial grades of this ore contain approximately 4% beryllium. The yearly consumption in the United States is at the present time 2500 to 3000 tons of beryl.

The principal producers of beryl ore are Brazil, Union of South Africa, Southern Rhodesia and India. Minor producers are British East Africa, French Morocco, Mozambique, Portugal, Canada and the United States of America. The availability of beryl ore has always exceeded the industrial demand and during the last two or three years the imports to the United States have been two to three times greater than the amount consumed by the beryllium industry. The excess imports have been stock piled by the Government and the industries.

PRODUCTION OF BERYLLIUM OXIDE

Beryl ore is an inert mineral and can be chemically attacked only at elevated temperatures. There are two commercial processes in use for recovering beryllium oxide from beryl, both of which involve aqueous chemistry. The one process uses fluoride as the vehicle and the other uses sulfate.

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In the fluoride process[5] which is used by the Beryllium Corporation, Reading, Pennsylvania, finely pulverized beryl is mixed with sodium ferric fluoride, sodium fluosilicate and soda and heated in briquette form to a temperature of 750°C. This treatment converts approximately 90% of the beryllium content in the beryl ore to sodium beryllium fluoride, which is leached out with water, leaving silica, aluminum oxide and iron oxide as an insoluble residue. The solution of sodium beryllium fluoride so formed is treated with caustic soda to produce a granular grade of beryllium hydroxide which is easily separated by filtration and washing. The filtrate from this operation which contains sodium fluoride is treated with ferric sulphate in order to recover the fluorine content as insoluble sodium ferric fluoride. This compound is separated by filtration, recycled and used again in the process. The beryllium hydroxide produced is calcined to oxide by heating to about 1000°C. The purity of this oxide is sufficiently high for direct use in the production of beryllium-copper alloy, but is not suited for refractory purposes mainly due to its sodium fluoride content.

The sulphate process[6] used by the Brush Beryllium Company is based on the discovery that if beryl is first completely melted without addition of chemicals or fluxes and then quenched in cold water, the resulting glassy beryl frit becomes reactive to sulfuric acid. The fusion is carried out at about 1700°C in a carbon-lined three-phase electric furnace, using the resistance of the molten ore to produce the required heat. The frit produced by the melting and quenching operations is further dried and heat treated in a gas-fired rotary kiln at temperatures between 900–950°C to increase the reactivity of the ore.

After heat treatment, the frit is ground to — 200 mesh and mixed to a slurry with 93% sulfuric acid in an amount chemically equivalent to the beryllium and aluminum content of the ore. The slurry is squirted in a small stream into a gas-fired rotating steel mill which is heated to high enough temperatures to convert the silicic acid formed into insoluble silica. The soluble beryllium and aluminum sulfates are then extracted with water leaving the insoluble silica behind. The sulphate leach liquor, which contains approximately 90% of the beryllium in the ore, and an excess of sulfuric acid corresponding to about one normal, also contains aluminum, iron and other impurities. The bulk of the aluminum is removed by adding ammonium hydroxide. The resultant ammonium sulphate converts the aluminum present to ammonium alum which has sufficiently low solubility at room temperature to crystallize out. The alum crystals are separated continuously in a centrifugal leaving a mother liquor of crude beryllium sulphate contaminated with aluminum, iron, etc.

Following the alum separation, sequestrants are added to the mother liquor to hold the undesirable impurities present in the solution, while an excess of sodium hydroxide is added to convert the aluminum and beryllium sulphates to aluminate and beryllate. Both of these compounds are quite soluble in cold alkaline solution, but they differ in that the beryllate decomposes on boiling to precipitate a granular form of beryllium hydroxide, whereas the aluminate is unaffected by boiling. This difference makes possible the precipitation of beryllium hydroxide without serious contamination by aluminum.

In practice, proportioned streams of a suitable chelating reagent such as ethylene diamine tetra-acetic acid and dilute sodium hydroxide solution are added continuously to the mother liquor remaining after the alum separation and the alkaline solution so formed is continuously decomposed in a hydrolyzer held at boiling temperature. The formed beryllium hydroxide is continuously separated and washed in a solid bowl centrifugal.

The standard grade beryllium hydroxide produced by this process contains between 5% and 15% moisture and on a beryllium oxide basis approximately 0.05% iron, 0.15% aluminum, 0.05% silicon and 0.15% sodium.

The hydroxide is converted to beryllium oxide by heating to approximately 800°C. Similarly to the grade of oxide produced by the fluoride process, the grade of beryllium oxide produced, as described above, is of sufficient purity to be used directly for the production of beryllium copper, but is unsuitable for refractory use mainly due to its sodium content.

In order to produce a highly refractory grade of beryllium oxide suitable for nuclear use, the Brush Beryllium Company's practice is to dissolve the beryllium hydroxide formed by the hydrolysis referred to above in sulfuric acid, whereupon ammonium sulphate is added to separate the remaining aluminum content. Practically complete separation of ammonium alum takes place when the concentrations are adjusted so that the beryllium sulphate solution is saturated at room temperature when an excess amount of ammonium sulphate is present. After removing the alum crystals, the beryllium sulphate in the mother liquor is crystallized by evaporation and cooling. The beryllium sulphate formed in this manner is of very high purity. It is converted to beryllium oxide by calcining to approximately 1150°C. The pure oxide produced at this temperature is fluffy in appearance, and contains only small amounts of alkalies.

FABRICATION OF BERYLLIUM OXIDE

Beryllium oxide for fabricating refractories is used as produced in calcined form in hot pressing, or it is fused for extrusion, dust pressing or slip casting. In fusing, the temperature is so high that it is necessary to protect the melt by providing the furnace with a lining of beryllium oxide itself. In the process developed by the Clifton Products Company the fusion is carried out in a single phase electric arc furnace using a power input of 250 to 300 kw. After fusing about 80 pounds of oxide the melt is allowed to cool until solid and is then removed from the furnace, cooled in the air, broken into pieces, and crushed in a jaw crusher. The crushed

material is then ground, screened and passed over a magnet to remove iron. After this treatment the material is ground wet in a small iron ball mill and then treated with a mixture of aqua regia containing free chlorine. The cleaned oxide is then separated by filtration, washed, dried with steam and finally heated in a muffle furnace to remove adhering particles of graphite from the electrodes.

Fluffy, calcined beryllium oxide is usually fabricated by pressing in graphite dies at 1600°C to 2300°C, applying pressures of 500 to 200 psi. This method developed by the Norton Company produces oxide blocks of density approaching the maximum theoretical and develops the optimum properties of beryllium oxide. When fabricated in this manner further operations are not generally required, except when firing is required for whitening or grinding and sawing needed to finish the body to very accurate dimensions. Diamond tools are required for sizing high density beryllium oxide blocks making direct fabrication to final contour and dimension very desirable.

Conventional ceramic operations can also be used with high fired, or fused beryllium oxide. Such operations involve dust pressing, slip casting, ramming and extrusion. In order to provide strength for handling before firing, bonding materials such as paraffin, starch and resins are useful. If machining operations are needed, it is preferable to prefire the refractory body at 1200–1500°C and to do the machining before the final firing at 1700°C to 2000°C. These machining operations are done with carbide tools. The densities produced vary between 2.0 to 2.6 grams per cm^3, depending upon the firing temperature, the purity of the oxide and the particle size. For making intricate parts dust pressing and firing operations may be especially attractive as fused beryllia may be cold pressed to desired density and fired without shrinkage. Sometimes small amounts of alumina, silica, and calcium oxide are added if strength and density are more important than the refractory properties. To serve as a binder, an addition of beryllium sulphate to fluffy beryllium oxide may also be useful before firing. After firing at low temperature, the porous refractory body is then impregnated with another mixture of fluffy oxide and beryllium sulphate before refiring at a higher temperature.

REACTOR USE OF BeO

Beryllium oxide is about as good as beryllium metal as a moderator when considered from a nuclear standpoint. In addition it is chemically inert and has a high melting point. It therefore seems particularly attractive for use in a high temperature air-cooled reactor. Unfortunately the oxide, in common with other ceramics, is very brittle and therefore is not easily adopted to engineering use. There are no reactors in the USA which use BeO as a moderator.

Extensive work has been done to evaluate and improve the ability of BeO to withstand thermal stress at elevated temperatures. One of the principle test procedures consists of generating heat inside a long tube of the oxide of accurately controlled dimensions and determining the heat flux and temperature at which the tube cracks. Investigations by H. Schofield at Battelle Memorial Institute and W. Galbreath at Oak Ridge National Laboratory have shown that the thermal rupture resistance may be substantially improved by small additions of Al_2O_3 or ZrO_2 and by controlled porosity. Unfortunately the reactor builders want as high density as possible.

The thermal conductivity of BeO is unusually high and this is a factor in its favor. However, the conductivity decreases with increasing temperature as shown in Table I.

Table I. Thermal Conductivity of BeO

Temperature, °C	*K watts-cm/cm²°C*
540	0.34
760	0.24
980	0.17

In addition it has been found that fast neutron irradiation decreases the conductivity. In one case after a total flux exposure of 1.3×10^{20} nvt the conductivity at room temperature was decreased by about 40%.

BeO could be used in a low power reactor but further improvement in thermal rupture behavior is required before it can be employed in a high performance reactor.

PRODUCTION OF BERYLLIUM METAL

The bulk of the pure beryllium metal produced in the United States is made by the reduction of beryllium fluoride with magnesium metal by a process developed by the Brush Beryllium Company.[7] This process can be divided into four basic steps: (1) production of high purity ammonium beryllium fluoride salt; (2) thermal decomposition of ammonium fluoride to beryllium fluoride; (3) reduction of beryllium fluoride to beryllium metal with a stoichiometric deficiency of magnesium metal; and (4) vacuum casting.

Ammonium Beryllium Fluoride

This salt is produced by dissolving beryllium hydroxide, beryllium oxide, or beryllium scrap in ammonium bifluoride solution. This solution is purified by adding lead dioxide to precepitate manganese and chromium by oxidation. Aluminum is precipitated on the addition of calcium carbonate which raises the solution pH to approximately 8.3. No beryllium is precipitated by this treatment since ammonium beryllium fluoride does not dissociate to any great extent. Following filtration to remove the lead, chromium, manganese and aluminum, other metals which may be present in small amounts are precipitated as sulfides. The remaining filtrate is then evaporated and crystallized in a continuous vacuum salting evaporator. The salt so produced contains only trace amounts of impurities.

Beryllium Fluoride

Ammonium beryllium fluoride salt is readily decomposed at temperature in the range of 900°C to 1100°C to ammonium fluoride and beryllium fluoride.

The salt is fed continuously into the top of the furnace and liquid beryllium fluoride is continually drained off through an overflow weir at the bottom of the furnace. The ammonium fluoride gas is taken off at the top and absorbed in a scrubbing tower. The ammonium fluoride solution so formed is recycled to the dissolving operation and the beryllium fluoride pebbles are stored for the reduction process.

Metal Reduction

Beryllium fluoride is readily reduced by magnesium at temperatures close to the melting point of beryllium fluoride. If stoichiometric proportions of fluoride and magnesium are used, an effective separation of the metal is difficult due to the high melting point of the magnesium fluoride slag formed. It is, therefore, necessary to add a fluxing material to lower the melting point of the slag and to produce a very liquid slag so that the metal can readily float and conglomerate. In the practice developed by the Brush Beryllium Company it was found that beryllium fluoride itself is the best and the most economic flux to use. For this reason an amount of magnesium is added to the fluoride corresponding to approximately only 75% of the amount required stoichiometrically. Another advantage in using an excess amount of beryllium fluoride is that the beryllium fluoride remaining in the slag after the reduction is easily leached out with water leaving a residue of insoluble magnesium fluoride. The beryllium fluoride solution is recycled to the ammonium beryllium fluoride production step.

In practice, the beryllium fluoride reduction is carried out in a 100 kw, 3000-cycle high frequency electric furnace provided with a graphite crucible. After completing the reaction at about 900°C the temperature is raised to the melting point of beryllium and the molten mixture is then poured into a receiving pot and allowed to cool. The entire solid block of metal and slag is then charged into a stainless steel ball mill and wet milled in order to separate the beryllium metal pebbles from the slag.

The over-all beryllium recovery in the reduction of the milling operation is between 96% and 97%.

Beryllium metal pebbles produced by this process contain approximately 97% beryllium with a total metallic impurities content, exclusive of magnesium, of from 0.2% to 0.5%. The beryllium oxide content is about 0.1%; the balance is slag.

Vacuum Casting

The pebbles produced as above contain some slag and are melted for purification in a 100 kw, 3000-cycle high frequency electric furnace operated in a vacuum of approximately 300 microns. Both the melting crucible and the mold are contained within the evacuated space. The crucible is made of beryllium oxide and the mold of graphite. The average size casting is 70 to 75 pounds and the operating cycle is five hours.

The complete analysis of a vacuum casting typical of metal produced by Brush is: % Be, 99.5; ppm C, 400; ppm Fe, 1100; ppm Mn, 70; ppm Cr, 90; ppm Ni, 130; ppm Mg, 500; ppm Al, 600; ppm B, 1.2; ppm Cd, 0.5; ppm Li, 1; ppm Ag, 5; and ppm Co, approx. 2.

ELECTROLYSIS OF BERYLLIUM CHLORIDE

The problem of electrolyzing beryllium chloride has been studied for many years and in fact, was one of the earliest methods for producing beryllium on a laboratory scale.

The electrolyzer may consist of a nickel pot serving as the cathode and a graphite electrode serving as the anode. The pot should be tightly covered to exclude air. At the same time the cover must be provided with an opening for the anode, an inlet for hydrogen or other inert gases if such gases are used, and an outlet for the chlorine gas produced and the inert gas if used. The temperature of the electrolyte may be maintained by heating the nickel pot externally.

Since beryllium chloride itself is a non-conductor, the electrolysis is generally carried out in the presence of sodium chloride or other alkali chlorides. The temperature of the electrolyte varies in accordance with the alkali fluoride additions. Using sodium chloride alone the temperature of the electrolyte is approximately 730°C and the voltage applied is a minimum of five volts. Electrolytes containing a eutectic mixture of several alkali chlorides such as used by Brush in the early period of developing processes for producing beryllium can be electrolyzed at temperatures as low as 400°C if the beryllium chloride concentration is maintained.

The beryllium formed is deposited in flake form on the inner wall of the nickel pot and is removed after completion of the run. The flakes which are always covered with a layer of fused salt are generally leached with cold water and finally washed in a filter with water and alcohol and dried at a low temperature to avoid excessive oxidation. In the method developed by the Clifton Products Company the flake is washed with sodium hydroxide solution and then with dilute nitric acid.[8]

Although extremely pure beryllium can be produced by this method, experience has so far indicated that beryllium powder made from flakes contains enough slag to produce some difficulties in fabrication. Beryllium chloride is also extremely hydroscopic and therefore tends to hydrolyze into beryllium oxychloride which is insoluble in the electrolyte. The process so far has not been developed to a point where it competes technically or economically with the direct reduction of beryllium fluoride with magnesium.

MELTING AND CASTING

It is customary to melt beryllium in vacuum and to use BeO crucibles. The vacuum is required not

merely to minimize oxidation but also to remove volatile constituents such as magnesium, sodium, and various fluorides and chlorides. BeO crucibles are required because the metal will react to a certain extent with all other stable oxides, especially in vacuum.

Equipment for vacuum melting beryllium on a commercial scale has been described elsewhere.[2] In order to make high quality castings it is desirable to use a stopper rod and pour from a bottom hole. The reason for this is that when metal is poured from the top of the crucible it flows over some of the condensed volatiles and the resultant casting may contain porosity. As already mentioned, the Brush Beryllium Company crude pebble is vacuum melted in a tilting furnace but the only objective of the operation is to remove impurities prior to converting the metal to powder.

Melting of beryllium in an open pot has been extensively studied.[9] It is extremely difficult to avoid porosity in the casting due to hydrogen evolution during solidification. The hydrogen presumably comes from reaction with atmospheric moisture. In addition the removal of magnesium is incomplete and the oxidation losses are excessive.

A sound casting requires the use of a clean, gas-free mold to avoid a scabby surface due to mold outgassing. Graphite is suitable for this purpose providing that it is first baked out in vacuum and is not exposed to moist air when not in use. The wall thickness of the graphite must be carefully chosen since beryllium carbide will form if the mold becomes too hot while cracking of the metal occurs if the cooling rate is excessive. It has been found that castings more than 6 in. in diameter almost invariably contain fine cracks at the central axis. The addition of about ½ per cent of aluminum helps to avoid this. It is advantageous to use a hot top made of alundum or beryllium oxide in order to reduce the amount of pipe. It is undesirable to use ceramic molds because the slow cooling rate leads to excessively coarse crystals.

Beryllium castings have been used only for producing extrusion billets. The metal as-cast is exceedingly brittle, largely because of the coarse grain size. A casting of intricate shape would almost certainly contain internal cracks at the regions where the columnar grains meet. The machining characteristics of a casting are poor because the hardness of individual crystals is quite anisotropic and in addition surface cracks form readily. These difficulties could be avoided if the casting could be made sufficiently fine grained. It has not been possible as yet to get extensive grain refinement by small alloy additions. There is a considerable incentive to achieve fine-grained castings since the cast metal is much less expensive than the powder metallurgy product.

PHYSICAL METALLURGY

The physical metallurgy of beryllium has been extensively studied in an effort to improve the ductility.[3] The first line of attack has been to try to determine if an impurity is responsible for the brittleness. Metal having an impurity content of (in parts per million) 50 Al, 50 Ca, 50 Cr, 110 Cu, 50 Fe, 35 Mg, 35 Mn, 100 Ni, 50 Si, 300 C, 18 N, 100 Cl, 1000 O can be produced by vacuum melting of electrolytic flake. This metal is no more ductile than less pure forms of beryllium. Distilled beryllium has been made by Kroll[10] and by various workers at M.I.T. without improvement of the ductility. There appears to be little hope that further removal of metallic impurities will give ductility. There has always been question that oxygen causes the brittleness but no one has been able to establish that oxygen is soluble in the solid metal or that removal of oxygen gives improved ductility. Vacuum-melted beryllium appears to contain less oxygen than any other form of the metal and yet it is the least ductile.

Allowing of beryllium offers little promise of producing a more ductile metal.[3,11] There are very few elements having appreciable solid solubility in beryllium and each of these appears to make the metal more brittle. There is no reason to believe that beryllium can be deoxidized by alloy additions and experiments along this line have led nowhere.

A number of investigators have reported a double heat effect at the melting point of beryllium.[12] The upper effect is at about 1278°C and the lower one at 1262°C. Even the purest beryllium available shows this phenomenon. Work is in progress to try to definitely prove whether this is caused by some impurity or whether it is a phase transformation.

It has been known for some time that fabricated beryllium can display fairly large ductility in the fabrication direction. Recent work on deformation of beryllium single crystals has provided a clear explanation of this. It is found that beryllium can slip almost without limit on the $10\bar{1}0$ prism planes.[13] The critical resolved shear stress at room temperature is about 9500 psi. Slip also occurs on the basal plane at about one third of the stress for prism slip but fracture always occurs on the basal plane shortly after slip has started. It is this easy fracture on the basal plane which is primarily responsible for the brittleness. Beryllium can twin on the $10\bar{1}2$ plane under tensile stress parallel to the C axis. Fracture can occur on the twin interface and also on $11\bar{2}0$ prism planes but these fracture modes are not nearly as important as that of the basal plane.

The ductility which can be achieved in polycrystalline commercial beryllium is closely related to grain size. For this reason the recrystallization and grain growth behavior of beryllium is of importance. Recent work[14] has shown that the recrystallization of beryllium follows about the same pattern as for other metals. It is found that simple deformations such as slip and twinning in single crystals do not lead to the appearance of new grains upon annealing. Kinking is very prevalent in polycrystalline beryllium deformed at elevated temperatures. Annealing of kinked regions leads to polygonization with numer-

ous small angle boundaries. These subgrains are usually fairly large in size and constitute a structure which does not disappear readily upon further annealing. With sufficient heating the orientation difference between the subgrains becomes gradually larger so that well annealed, equiaxed grains finally are established. This behavior makes it impossible to get a really fine grain size by working and annealing of vacuum cast metal. It also means that the preferred orientation developed by deformation tends to persist even after extensive annealing. Powder metallurgy beryllium can have a much finer grain size than fabricated cast metal because the oxide film on each powder particle inhibits grain growth.

FABRICATION TECHNIQUES

Hot Extrusion

It is customary to extrude beryllium in the temperature range between 900°C and 1100°C. This temperature is required both because the minimum recrystallization temperature is about 750°C and because the metal is quite stiff. At 1000°C a unit pressure of about 55 tons per square inch is required to achieve a reduction in area of 25 times. Beryllium has a pronounced tendency to stick to most die materials. For this reason it is customary to surround the billet with a shell of low carbon steel which extrudes along with the beryllium. A lubricant of powdered graphite in heavy oil is quite satisfactory. In order to ensure a uniform flow of the steel it is necessary to use a conical approach to the die. A heated graphite disc of 3 to 4 in. thickness is placed behind the beryllium billet in order to expel all the metal from the machine. This procedure eliminates the problem of cutting off an extrusion butt.

The high temperatures, heavy pressures, and the use of a steel clad make it difficult to produce extrusions of complicated cross section. Satisfactory round bars and flat shapes can be made. Tubes have been produced but mandrel failure is liable to occur for inside diameters of less than about one-half inch.

It is possible to extrude chips, electrolytic flake or fine powder using the same techniques. It is desirable to cold compact the material in the steel can to as high density as possible before extrusion. This is necessary in order that the steel can does not develop folds during the initial consolidation at the beginning of the extrusion. It is desirable to evacuate and weld shut the steel can in order to avoid oxygen and nitrogen pickup by the beryllium powder.

The steel sheathing can be removed by peeling or by pickling in strong nitric acid. The surface of the beryllium is more or less rough depending on the starting material. A cast billet gives a serrated, bark-like surface on the extrusion due to the fact that various grains indent the steel cladding by different amounts. An extrusion of 200 mesh powder has a smooth, silky appearance but the diameter may be somewhat variable along the length depending on how uniformly the steel flowed. The yield of good metal is about 80 to 90%.

Rolling

Hot rolling is carried out at 800°C to 1100°C using a steel sheath on the beryllium. A steel thickness of about ¼ inch is satisfactory for a total reduction in thickness up to 90%. It is usually desirable to reheat the sheet after one or two passes. The surface smoothness of the final sheet is greater the finer the original grain size. Extruded powder is particularly suitable for rolling. Sheet as thin as 0.005 in. can be produced if sufficient care is used. Thin sheet can be rolled bare at about 300°C especially if heated rolls are used.

Forging

It is possible to deform beryllium at 600°C to 1000°C by press forging inside of a heavy steel shell. A single stroke operation is more successful than a series of deformations. Die forging of bare metal at about 1000°C can be carried out providing that the metal is not subjected to extensive tensile deformation.

Discussion

It is generally found that beryllium deformed at temperatures as high as 1000°C and then air cooled will not be in a fully recrystallized, equiaxed condition. Subsequent annealing is not necessarily desirable, however, unless the crystals are in a severely deformed state.

POWDER METALLURGY[16]

Powdering

Beryllium powder of the Brush type is produced by comminution of 50 to 70-pound vacuum cast ingots to chips, using a multiple turning operation. These chips are fed into a water-cooled beryllium-faced attrition mill operating in an atmosphere of dry nitrogen. Powder from this mill is passed over a vibrating screen to remove the —200 mesh fraction, with the oversize powder being returned to the top of the mill for regrinding. Commercial beryllium powder is sized through the 200 mesh screen and consists of about half —200 + 325 mesh and half —325 mesh by weight. Despite the dry atmosphere, the beryllium oxide content of the powder increases from about 0.1% to 0.2% in the vacuum-cast metal to 0.3% in chips, and to about 0.7% to 1% in the finished —200 mesh powder.

The beryllium oxide content of powder is a function of particle size, increasing with diminishing particle size. However, beryllium oxide is advantageous in controlling grain size during sintering, as the barrier effect on grain boundaries of the oxide retards normal growth until rapid grain growth occurs at temperatures greater than those normally approached during fabrication.[17] Despite the increasing oxide content, fine grain beryllium requires less pressure for densification than coarse grained metal and shows superior mechanical properties at room temperature. However, at temperatures above 500°C, where grain boundary failure occurs under mechanical loading, the coarse, or lower surface, particles

give better mechanical properties. As an effective compromise between all of these variations, the commercial —200 mesh powder averaging around 20 microns in particle size (ranging from 2 to 200 microns) has been chosen. In this form, beryllium powder can be stored without special precautions in glass bottles for long periods of time without appreciable moisture pickup or deterioration. However, it has been noted that powders made by other methods, notably those containing chloride, either reduced by thermic or electrolytic methods and containing residual slag, not only suffer considerable deterioration on standing, but are difficult to attrition and fabricate.

Consolidation of Powder

Beryllium powder is consolidated to full density by a number of methods, including (1) cold-pressing, sintering, and mechanical deformation, (2) vacuum hot-pressing, (3) warm or hot-pressing under atmosphere pressure, and (4) hot working of beryllium powder in metal cans.

If a large number of small uniform parts are desired, beryllium can be cold-pressed at 40-100 tsi, sintered at 1050–1150°C, and coined, rolled, or extruded to final density at 400–500°C. Although this temperature spread for coining is considerably below the recrystallization temperature range for beryllium, it is above the brittle-ductile mechanical transition which the metal undergoes. At these temperatures beryllium has considerable ductility, the hot-pressed material showing up to 50% elongation or tensile contraction in area in all directions (isotropic) over the temperature range 300–500°CC.

The principal advantage of processing in the warm range is in obtaining contours and dimensions very close to the as-finished condition, although high pressures needed to operate in this temperature range (20–80 tsi) limit the process at the present time to small objects. Warm processing has been used in forging, coining, rolling, and extruding sintered beryllium to final shape and density. Warm pressing, wherein the powder may be fabricated to full density by simultaneous application of heat and pressure at a temperature around 450°C, is not used commercially because, without sintering above the recrystallization temperature, beryllium is extremely brittle and lacks dimensional stability even though it has been brought to full density.[16]

One of the most widely used methods of fabricating large fine-grained blocks of beryllium is vacuum hot-pressing, wherein full density is obtained at 1050–1150°C under pressure of 75–100 psi and upwards. In this operation, either steel or graphite molds are used, depending on shape and pressure desired. The molds are filled with powder usually by vibrating the molds to secure even compaction. Because of the large masses of powder used (several hundred pounds) and the low pressures employed, a relatively large time cycle (4 to 20 hours) is needed. Higher pressures, if allowable by the mold materials, will diminish the time cycle, but higher pressure usually gives anisotropic mechanical properties to the metal. One of the major advantages of vacuum hot-pressing is the uniformity of properties in all directions, unlike practically any other method of fabrication.

So-called direct pressing, wherein bodies are pressed to density at 1000–1250°C under normal or protective atmospheres, has been used, but is considered unreliable, especially for large bodies, because of potential die failure, as pressures from 1000 to 2000 psi are needed to obtain full density. Should suitable die materials be developed, this method would be very interesting because of its potential for rapidly producing shapes close to finished dimensions.

A modification of hot-pressing of the vacuum type is high temperature hydrostatic or pneumostatic hot-pressing, or what has been referred to as the "envelope technique." The vacuum envelope pressing technique was developed chiefly for producing dense intricate bodies under pressures from 100–300 psi and temperatures from 1000–1100°C. A thin-walled steel form whose internal surface is contoured to the desired shape contains the beryllium, and the entire assembly is placed inside a heated pressure vessel. The intervening positioning of the sintering assembly is accomplished through filling the space between the pressure vessel walls and the assembly with a non-sintering permeable ceramic powder and pressurized with inert gas. The steel can or form containing the beryllium powder is then evacuated and the assembly brought to temperature. In this manner, long thin tubes, rods with irregular cross sections, and special shapes can be produced, close to full density, for use or final dimensioning by light deformation.

Another method of fabricating beryllium powder is to contain the powder in a steel protecting can in which the powder is either vibrated or cold-pressed to obtain as great a fill as possible. At temperatures above the recrystallization range, the beryllium can then be rolled, forged, or extruded to density and shape with pressures of 2000 to 10,000 psi, in a temperature range of 900° to 1100°C.

DUCTILITY OF FABRICATED BERYLLIUM[18]

The observed facts with regard to ductility of commercial beryllium are:

1. A cast single crystal can slip extensively on $10\bar{1}0$ planes, twin on $10\bar{1}2$ planes, and fracture on 0001, $11\bar{2}0$, and $10\bar{1}2$ planes.
2. Cast polycrystalline beryllium exhibits essentially zero elongation in tension at room temperature.
3. Extruded castings have 2 to 3% elongation parallel to the extrusion axis and are brittle in a transverse direction.
4. Hot-pressed 200 mesh powder has about 2% elongation in all directions.
5. Extruded 200 mesh powder has 15 to 20% elongation in a parallel direction and 1 to 2% perpendicular thereto.
6. Extruded 200 mesh powder cross rolled at 1000°C with 6 to 10 times reductions has 30 to 40% elongation in all directions in the plane of the sheet.

All of these materials have essentially the same purity except that metal derived from castings has about 0.2% oxygen whereas metal made from powder has about 1% oxygen.

The differences in ductility are a function of preferred orientation and grain size. It is clear that a specimen having all the crystals oriented with the basal planes parallel to the stress axis should resist fracture and should be able to elongate by slip on the prism planes. This texture is produced in hot working and is the principle reason why some ductility is found in fabricated beryllium. It is necessary, however, to also consider grain size in order to understand the differences mentioned above.

The importance of grain size is illustrated by the different ductility of cast and powder metallurgy beryllium. In each case the grains are more or less randomly oriented but for the cast metal the grain size is usually 1 to 10 mm in diameter while the hot pressed material has grains of about 0.002 to 0.2 mm. In each case there will be some grains unfavorably oriented with respect to the stress axis and easy fracture should occur. Apparently with smaller grains the propagation of fracture is inhibited to a substantial extent. Various experiments seem to indicate that the oxide film which existed around each powder particle before hot pressing does not contribute directly to the improved ductility. This film is of importance, however, in preventing grain growth during the sintering operation.

The difference in ductility between extruded cast and extruded 200 mesh powder again illustrates the importance of grain size. Careful measurements have shown that the statistical texture can be made quantitatively identical in both cases, especially if the cast metal is water quenched at the extrusion exit. This texture consists of a $10\bar{1}0$ axis parallel to the extrusion direction with the 0001 axes of the various grains normal to this direction and randomly distributed about it. The extruded casting will have a grain size of 0.1 to 1 mm as compared with about 0.02 mm for the extruded powder. The grain size of the latter is even finer than the original 200 mesh size since each particle was elongated by a factor of 20 or more and the subsequent recrystallization, by and large, still takes place only within the elongated boundaries of each oxide envelope.

It is to be noted that in a rod extrusion the random distribution of the basal planes about the rod axis will not lead to the maximum possible elongation even though the prism planes are favorably oriented for slip. The reason for this is that prism plane slip does not lead to a dimensional change of the crystal along the C axis. Adjacent crystals therefore do not experience the same distortion in a direction perpendicular to the applied load and this leads to stress concentrations on a micro scale which eventually cause fracture.

The importance of this consideration is demonstrated by the extraordinary ductility of the cross-rolled sheet. In this case the basal planes can be made almost parallel with the plane of the sheet. This texture not only gives ductility in all directions in the plane of the sheet but tends to avoid stress concentrations between neighboring grains as the deformation proceeds. The sheet does not neck down perpendicular to its plane. Some work has been done to show that cross-rolled beryllium with the above described texture can have extensive ductility even though the grains are relatively large. Apparently the importance of grain size can be minimized if stress concentrations between adjacent crystals are avoided.

HIGH TEMPERATURE STRENGTH

It is well established[3, 17] that the tensile ductility of both extruded cast and powder metallurgy beryllium increases rapidly above room temperature. The maximum ductility occurs in the range of 300 to 500°C with elongations of 30 to 50%. At higher temperatures the elongation decreases in a somewhat erratic manner and becomes a function of the rate of elongation. This latter behavior apparently is caused by failure of the metal at the grain boundaries.

The strength of beryllium decreases rapidly with increasing temperature and is about half as great at 500°C as at 20°C. Above 500°C the strength becomes erratic depending on the strain rate. Some information on creep rate and stress-rupture life in the range 700°C to 1100°C has been obtained on extruded cast metal.[3] Further careful work would need to be done to get reliable engineering data.

A small amount of work has been done which indicates that the addition of BeO to powder metal in amounts of 5 to 25% can increase rupture life at high temperatures. It also appears that solid solution alloys such as 1% nickel can improve the high temperature behavior.

MACHINING

Beryllium produced by powder metallurgy techniques is machined readily and easily, using standard machining methods applied in the machining of heat treated cast aluminum and cast iron. Both cast and extruded cast beryllium are more difficult to machine.

The major problems in machining of beryllium are connected with the abrasive nature of the metal, the economic necessity of recovering clean dry chips and particles for recycling to powder production and the prevention of health hazards from atmospheric dispersion of beryllium dust in the working areas.

Although successful machining has been done using standard high speed tools, it is generally preferable to use tungsten carbide tipped tools. Lathe turning, milling, sawing, drilling, reaming, and grinding operations are all used with excellent results, although such operations as deep drilling are more complex. Standard grinding finishes using an open structure wheel are readily achieved while grinding wet. Some minor problems in grinding are due to the non-magnetic properties of beryllium.

Practically complete recovery of chips, particles and dust of beryllium resulting from dry machining operations are necessary both for economic and for health control reasons. The type of air exhaust equipment needed for these purposes must be highly efficient and is necessarily more complicated and expensive due to health control considerations than is required merely to recover chips, etc. for recycling.

Our experience gained from many years of continued beryllium machining operations indicates that such operations can be carried out safely and without danger to health.

It should be noted that the speed of removing beryllium metal in dry machining operations is governed by the efficiency of the exhaust equipment and not by the machinability of the metal.

CORROSION

Beryllium is quite corrosion resistant to air and water. High grade metal remains bright for years in the atmosphere at room temperature and does not oxidize appreciably even at 600°C. A heavy white oxide forms in about one hour at 900°C and very rapidly at 1000°C or higher. However, the metal does not burn in the sense that it raises its temperature above the surroundings. When beryllium does corrode at room temperature the difficulty can be traced to non-metallic inclusions such as carbide or chloride.

Aqueous corrosion of beryllium is sometimes erratic for reasons which are not well understood. The hot-pressed powder is much more consistent than cast metal and it appears that the difference in grain size may be partly responsible for this. It is found, for example, that a single crystal is destroyed completely in high temperature water by numerous cleavages along the basal plane even though only minor amounts of oxide have been formed. Some hot-pressed powder metal has been observed to corrode in demineralizde water at 100°C at the rate of about 0.1 to 1 mil per year with occasional pits of one to five mils in depth.[19] This corrosion behavior varies with the quality of the metal and it is believed that present production is better in this respect. Ions of chloride, sulphate, copper, and iron in the water increase the pitting rate somewhat. Commercial hot-pressed powder readily passes an acceptance test which involves exposure to 250°C water for 96 hours. Some of this same material has been found to be more corrosion resistant than zirconium in 350°C water but other samples disintegrate completely. The reasons for these differences are not yet understood but there is some evidence to show that aluminum and silicon impurities are harmful and that iron is beneficial.

Beryllium is not attacked appreciably by pure molten sodium at 500°C. Beryllium oxide does form in sodium at this temperature if the sodium contains more than about 0.01% oxygen.

There is no evidence of stress corrosion of beryllium either in high temperature water or in sodium.

IRRADIATION

All evidence to date indicates that beryllium metal is not appreciably altered by neutron irradiation. Specimens of cast and forged, cast and extruded, and extruded chips were exposed in a thermal reactor to an integrated flux of 1.8×10^{20} nvt. There was no change observed in dimensions, electrical resistivity, or corrosion resistance and only a slight increase in hardness and decrease in thermal conductivity. Hot-pressed powder metal made by the Brush process has been used successfully in the Materials Testing Reactor for a number of years.

BERYLLIUM HEALTH HAZARDS

Many years of industrial experience indicate that a potential health hazard exists in the handling and processing of beryllium and its compounds. At the same time practical methods have been developed whereby such hazards can be reduced or eliminated if proper precautions are taken.

It should always be kept in mind that the toxicity of any material depends on many factors, such as the amount and the concentration of the material involved, the time of contact, or exposure and the manner in which the body is exposed, such as skin contact, exposure of lungs and inhalation or ingestion through the mouth. As far as is known, no cases of digestive poisoning due to ingestion have been recorded in the beryllium industry, and no toxic effects have been reported as due to the mining of beryl ore, or the mechanical working or handling of low beryllium alloys.

However, soluble compounds of beryllium may cause dermatitis, and acute pneumonitis may be encountered when mists, dust, or fumes of beryllium-containing materials are inhaled.

Most medical authorities now also agree that beryllium containing mists, dust, or fumes may cause a delayed type of pneumonitis in individuals sensitive to beryllium. So far no method for testing an individual's sensitivity to beryllium has been found. The delayed type of pneumonitis also generally develops slowly and may extend over a period of many years. For these reasons, the practical difficulties involved in controlling the health hazard in the beryllium industry have been perhaps greater than for most other elements.

In practice the beryllium health hazard is effectively reduced or controlled by proper ventilation, frequent washing, and showers at the end of each shift. Personal cleanliness should be emphasized and the operator should be provided with a clean set of working clothes at the beginning of each shift. It is also advisable to have the chest of every employee checked at frequent intervals and to X-ray all employees at least once a year. In regard to ventilation, measures should be taken to control the volume of mists, dust, or fumes by enclosing and ventilating the equipment used and by monitoring the air both in the plant and in the vicinity of the plant for the

purpose of maintaining a safe level of beryllium content in the air.

A further discussion of this subject has been given by Merrill Eisenbud of the US Atomic Energy Commission.[20]

FUTURE OF BERYLLIUM

The successful development and growth of the beryllium industry during the last twenty-five years is mainly due to the unique capacity for precipitation hardening imparted by the addition of beryllium to heavy metals and particularly to certain copper base alloys, which have found many important applications in industry. The beryllium copper industry's earnings from beryllium copper have been a most important factor in reducing the cost of beryllium oxide and also made possible the development of processes for producing pure beryllium at a time when very little or no demand for the pure metal existed. The industry, therefore, could make imdiately available to the government pure beryllium in large enough quantities to meet early nuclear requirements for beryllium and at a cost much lower than would otherwise have been possible.

Later on with the development of nuclear energy the substantial investment of government funds in the development and improvement of production processes and fabrication methods has substantially contributed to the progress made in the pure beryllium field and in developing practical methods for controlling the health hazard. The beryllium copper industry is, however, bound to influence future prices of pure beryllium, since at the present time the major costs in producing the pure metal are due to the high unit costs of labor and general expenses resulting from low volume production.

The demand for beryllium and its alloys is steadily increasing due to the widening circle of industrial applications for its alloys and the growing interest for use of pure beryllium in nuclear applications. It can, therefore, be safely predicted that the beryllium industry will grow to a considerable size in the next 10 to 20 years.

The current ore supply of hand-cobbed beryl has always been more than sufficient to meet industrial demands and it is expected that even were substantially increased demands to occur, this type of ore supply will be sufficient for many years to come. It is, however, expected that the demand for beryllium in alloys and in nuclear applications will increase in the future to a point where the recovery of beryl from low grade beryllium deposits, which are now known to contain very large amounts of beryllium, will be necessary, as has been the experience in other industries. There are reasonable prospects that such recovery of beryllium-containing ores can be accomplished by concentration of low-grade beryl deposits although probably several years of development work is still needed.

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Sintering of Beryllium Oxide

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This study originated in a search for a process that would enable us to manufacture briquets of beryllium oxide of nuclear purity and of as high density as possible. The specifications were as follows:

1. The total cross section of the impurities for thermal neutrons must not exceed 2 millibarns, equivalent to 1800 ppm of iron in the beryllium oxide.
2. The density must at least equal or exceed 2.85 (theoretical density = 3.02).
3. The form adopted (rectangular parallelepiped 100 × 100 × 50 mm) must have dimensions accurate to 0.1 mm.

Preliminary study rapidly demonstrated that procedures now in use (natural sintering of a cast, tamped, or pressed form) to manufacture these briquets would entail great difficulty in turning out a product to meet the required specifications regularly.

We thought that sintering under pressure, introduced a few years ago[1], would be more effective. We ran a preliminary test on a laboratory scale to determine the potentialities of this technique in this particular case. Owing to the high toxicity of beryllium oxide, however, we preferred to determine the general sintering characteristics by using alumina.

We confined ourselves to checking the general results secured with the alumina by making a few tests with the beryllium oxide. Our results showed that the analogy was sufficiently reasonable. It actually enabled us to determine the manufacturing conditions required for a product that would meet the specifications prescribed.

SINTERING ALUMINA UNDER PRESSURE

Experimental Setup

The alumina powder was hot-compacted in a graphite mold (Fig. 1).

The sintering apparatus (Fig. 2) comprised a rigid frame, and a jack that enabled us to set up the desired pressure upon the product to be sintered via a column of aluminous refractories. A 0–6 ton dynamometer, located at the upper end of the framework and resting on the refractory column, measured the force applied to the table during sintering. The graphite mold was heated by induction. The high-frequency generator was of the spark type, rated at some 10 kva.

Temperature was measured by a Ribaud optical pyrometer. The precision of measurement, allowing for the various sources of error (regulation of the generator, definition of the brilliancy of the light source sighted on, etc.), was such that the temperature levels in the neighborhood of 1600°C were read to approximately ± 10 or 15°.

Raw Material

The alumina used is a variety of corundum. The content of the major impurities is as follows, expressed in terms of the Al_2O_3: Na, 31×10^{-4}; Cu, 10×10^{-4}; Fe, 7.75×10^{-4}; Si, 3×10^{-4}; and Mn, 0.5×10^{-4}.

The distribution of particle size, determined by sedimentation in a Martin balance, is as follows: $50 > \psi > 30$—5.3%; $30 > \psi > 20$—5.3%; $20 > \psi > 10$—34.8%; $10 > \psi > 5$—20.7%; and $\psi < 5$—33.7%. ψ is the mean diameter of the particles in microns. The size of the sample was 5 gm of powder.

Before sedimentation was measured dispersion was ensured by agitation for 24 hours in a liter of potassium pyrophosphate solution containing 1 gram per liter.

Preparation of Specimens

The alumina used was stored in a moisture-free place. Before being sintered under load it was compacted in the cold in a steel mold at a pressure of 2600 kg/cm².

All the experiments described in this paper were done with the crude tablets thus prepared, 30 mm in diameter, 14 mm thick, and weighing 18 gm. This is equivalent to an apparent density in the neighborhood of 1.8.

The tablets were dried in a drying oven at 120°C for 48 hours before sintering.

Sintering

The tablets were then placed in a graphite mold. At the start of the operation, a pressure of 30 kg/cm² was applied to the column to maintain the apparatus in place and to ensure adequate tightness to enable the stream of nitrogen that swept out the sighting channel to protect the graphite mold against too rapid combustion. The temperature rose to the neighborhood of 1600°C within 20 minutes. The sintering pressure was measured only after the experimental temperature had been reached. That pressure and temperature were kept constant throughout the sintering experiment.

Original language: French.

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Results

In view of the specifications prescribed for the proposed manufacture, we considered that the density of the product would be our principal sintering characteristic. We also determined the total and sealed porosity, though we regarded them merely as qualitative indications of the sintering process. As a matter of fact, by their very nature, these quantities cannot be determined very rigorously.

All other conditions remaining the same, especially the raw material, the form and the dimensions of the tablets, and the compacting of the latter in the mold, we may list the following physical factors as those affecting the sintering result: (1) the sintering temperature; (2) the time during which this temperature is maintained, and (3) the pressure at which sintering is performed.

Influence of Sintering Temperature

Figure 3 shows the variation of density and porosity with temperature for pressure of 200 kg/cm^2, applied for 30 minutes. In all these experiments, the initial sinking of the tablet under pressure was found to occur when the temperature reached 1150–1170°C. The three curves are linear between 1150 and 1320°C. Above the latter temperature the sealed porosity becomes the major factor, and increases in temperature give rise to a smaller increase in the density.

Above 1360°C microscopic examination of thin sections cut from the sintered sections exhibited the onset of recrystallization accompanied by slight orientation of the crystals parallel to the face under pressure. The higher the temperature, the more definite does the microcrystalline orientation become, particularly at the edges of the tablet. At 1450°C ($D = 3.79$) we find a slight increase in grain size

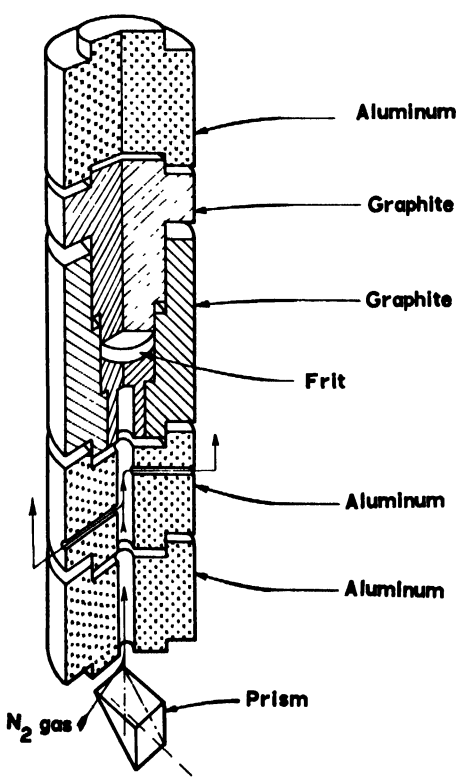

Figure 1. Column for sintering under pressure

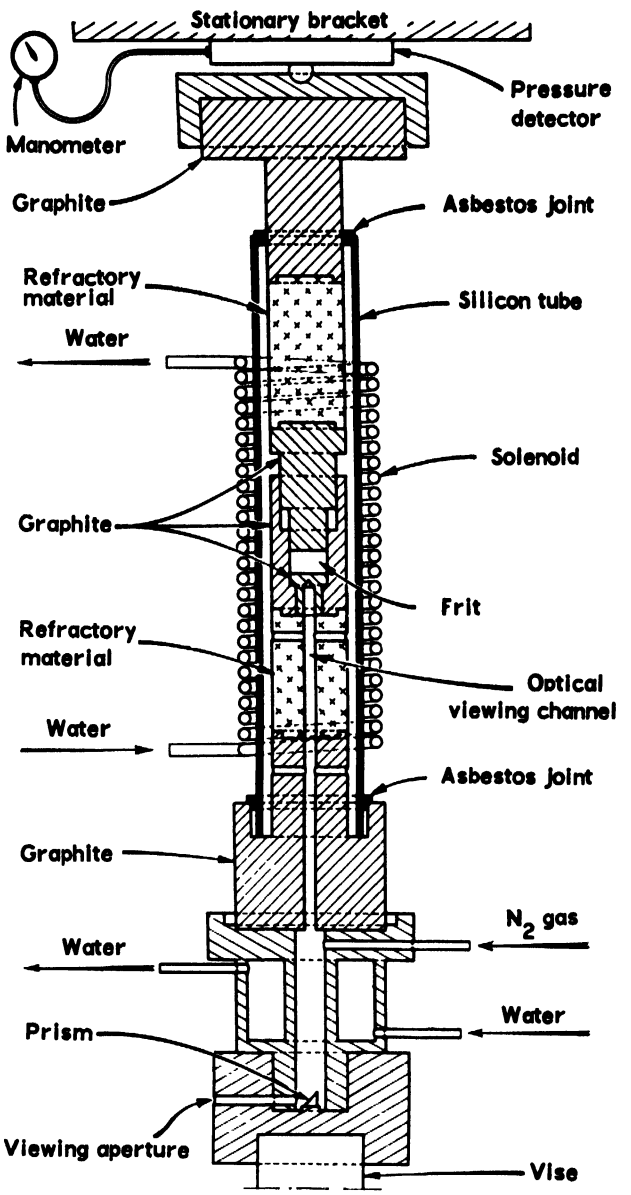

Figure 2. Sintering equipment

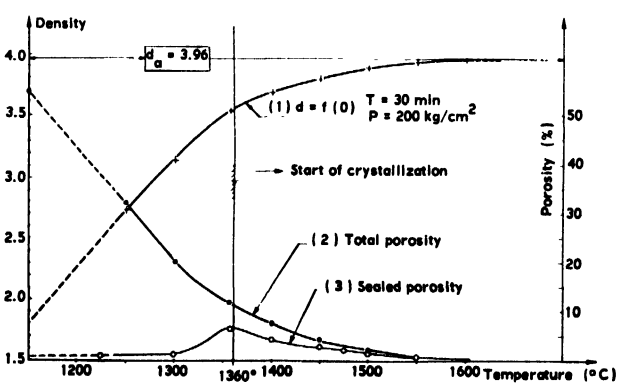

Figure 3. Curves

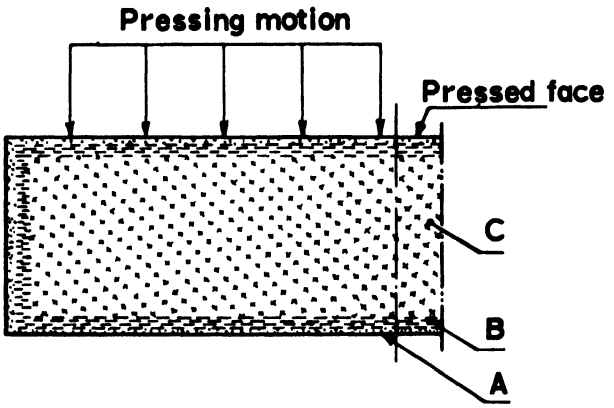

Figure 4. Crystalline zones

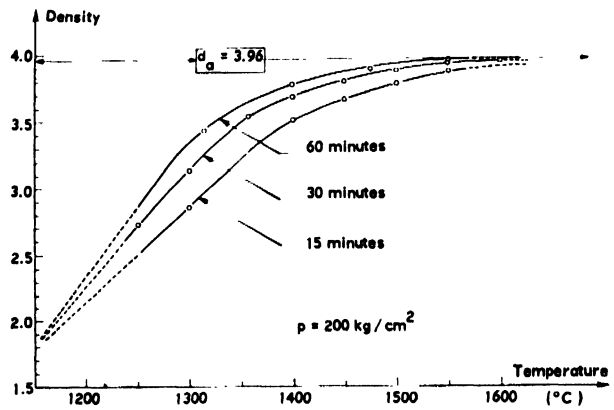

Figure 5. Curves of d = f (temperature) for different sintering times

at the edges. Finally, at 1500, 1550, and 1600°C each sintered tablet exhibits three crystalline zones (Fig. 4):

1. The first, Zone *A*, in contact with the graphite, consists of microcrystals. This zone extends to a thickness of 0.2 to 0.3 mm.

2. Zone *B*, on the other hand, consists of large crystals in the shape of lamellae parallel to the face under pressure. When the temperature rises from 1500 to 1600°C, the mean of the major dimension of these lamellae rises from 50 μ to over 200 μ. Under the same conditions the thickness of this zone increases from 0.4 to 0.7 mm.

3. Lastly, Zone *C*, comprising the interior of the tablet, is an aggregate of crystals ranging from 50 μ to 100 μ in size for the sintering temperatures of 1500 to 1600°C, respectively. Microscopic examination does not disclose any marked orientation.

We also investigated the effect of temperature upon the final density for sintering periods of 15 and 60 minutes. Our results are plotted in the curves of Fig. 5. The general course of the phenomenon remains the same. At a given temperature, we find that prolonging the time that pressure is applied increases the density. Prolonging the time of pressure application has less and less effect upon the density, however, as the temperature of the experiment is raised.

Above 1500°C the tablet becomes entirely gray. This is particularly marked in Zone *B* and may be due to slight contamination by the graphite.

Influence of Sintering Time

Our results are shown in the family of isothermal curves in Fig. 6. It does not seem feasible to attain the theoretical density at low temperatures. Moreover, sintering must be done at 1550°C, at least, to achieve a density in the neighborhood of 3.96.

Influence of Sintering Pressure

Our results are given by the points plotted in Fig. 7. These experiments were run at pressures ranging from 100 to 300 kg/cm² and at a temperature of 1400°C for 15 minutes. The density is almost a straight-line function of the pressure. Microscopic examination of thin sections cut from the

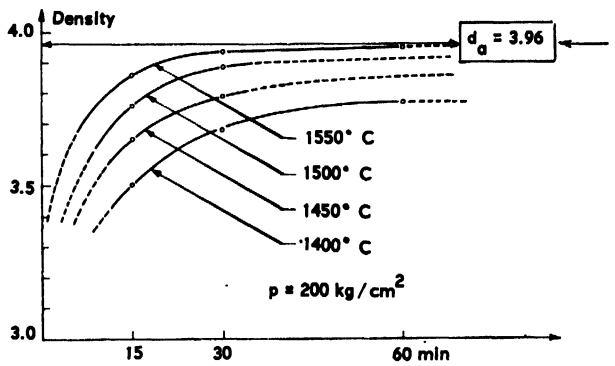

Figure 6. Curves of d = f (time) for different temperatures

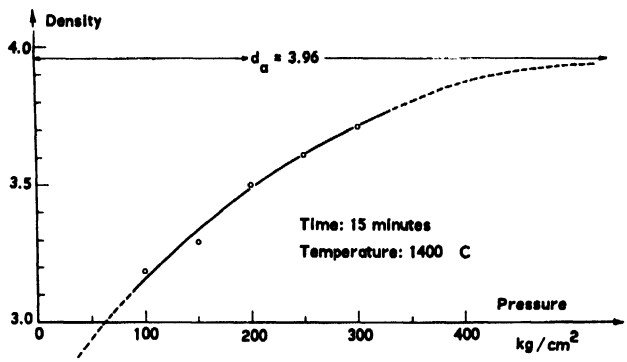

Figure 7. Curve of d = f (pressure)

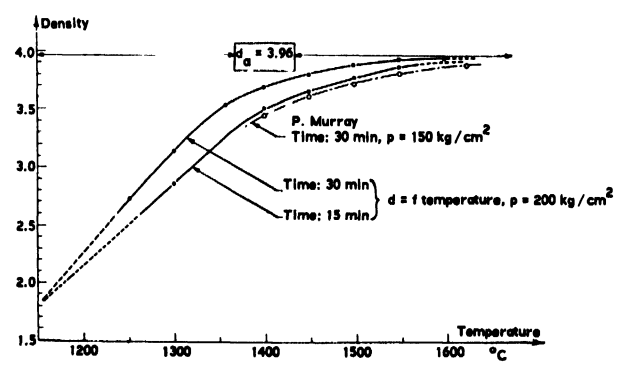

Figure 8. Curves

specimens discloses orientation of the crystallites in Zone A of the tablet after the 300 kg/cm² test.

Comparison of Our Results with Those Obtained by Murray

It is interesting to compare our results with those previously published by Murray and his co-workers.[2] In some of his experiments Murray employed an alumina produced by calcining ammonium alum and aluminum at 1000°. Sintering under pressure was likewise effected in a graphite mold under a pressure of 150 kg/cm², applied for 30 minutes. No analysis or particle-size distribution is given, though he probably used a very fine powder of high purity.

Our results may be compared by examining the curves of Fig 8. The parallelism of the curves is remarkable. The temperature difference may be due to the use of different pressures, though this factor is not the only one involved. As a matter of fact, the tablets sintered by Murray were thicker (2 cm in diameter and 1 cm thick), which affects the sintering results quite appreciably according to our experience.

SINTERING OF BERYLLIA UNDER PRESSURE IN THE LABORATORY

The experiments described above enabled us to develop the experimental setup and to mark out the general lines of sintering under pressure as applied to a pure oxide. Hence, all we required was a limited number of experiments with beryllium oxide, a product whose toxicity is well known, to determine its optimum sintering conditions. A density of 2.95 (theoretical density is 3.02) was obtained at 1600°C and at a pressure of 200 kg/cm² maintained for 30 minutes. This holds for tablets of the same shape as before and for a pure beryllium oxide produced by calcining $Be(OH)_2$. The total impurities in this oxide did not exceed 0.04%.

We have found that it is highly important to maintain extremely accurate precipitation and calcination conditions for the $Be(OH)_2$ if satisfactory results are to be obtained in sintering under pressure

FABRICATION

The material and the operations are similar to those just described on the laboratory scale. The graphite mold is designed to produce a sintered product 100 × 100 × 50 mm in size. The mold is heated by induction, using a 60-kva generator. The industrial process was developed in collaboration with Péchiney engineers.

Raw Material

We use beryllium oxide produced by calcining $Be(OH)_2$. This is done in large silica crucibles.

Sintering

The powder is put into the mold without any preliminary compacting. The sintering temperature is reached in one hour and a half. A pressure of 170 kg/cm² is applied gradually and maintained for 2 hours. The table on next page combines the results of several typical sintering tests. The shape of the sintered products makes temperatures in excess of 1600°C necessary for procedures to be completed within 4 hours.

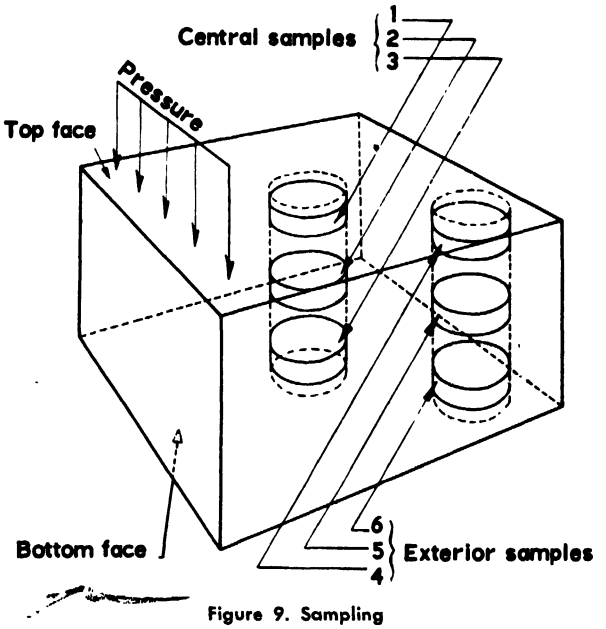

Figure 9. Sampling

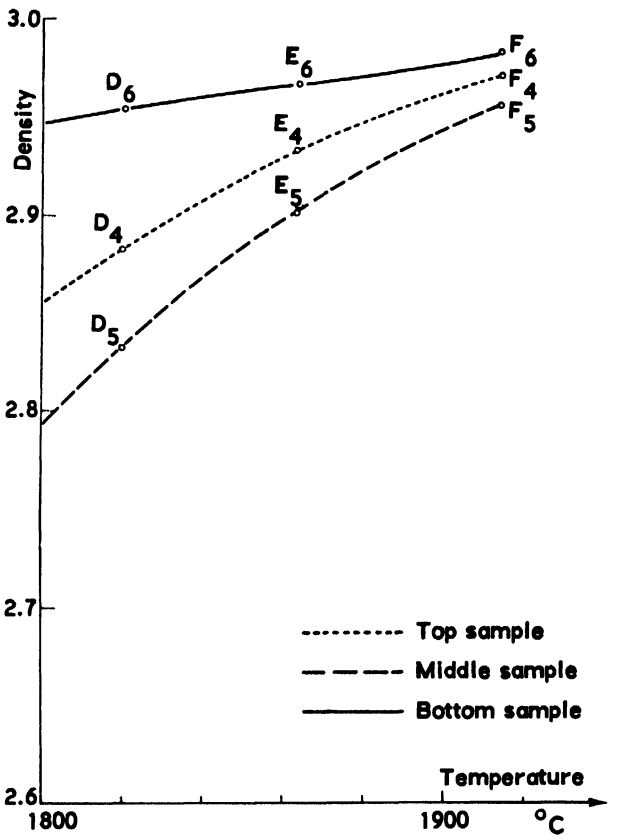

Figure 10. Distribution of density along the edges of the briquets

Six samples were taken from the briquets produced. Their location is shown in the diagram of Fig. 9. The densities measured in these samples are plotted in the curves of Figs. 10 and 11 for each temperature. The sintered products obtained, which were

Experiments	Temperature rise, hours	Sintering temperature, °C	Sintering pressure, kg/cm²	Constant temperature, hours	Mean density
A	1½	1700	150	2	2.70
B	1½	1720	150	2	2.79
C	1½	1780	150	2	2.82
D	1½	1820	150	2	2.86
E	1½	1850	150	2	2.90
F	1½	1910	150	2	2.94
G	1½	1760	170	2	2.91

very heterogeneous at low sintering temperatures, tend to grow uniform as the temperature is raised. Microscopic examination of thin sections cut from similar specimens, taken from a briquet that was sintered particularly well ($D = 2.98$) and of homogeneous density, exhibits some heterogeneity of crystallization however. The outer zone of the briquet consists of crystals that are much larger than those in the interior.

Results

The primary objective of this research has been to produce a few tons of briquets of pure beryllium oxide, 100 × 100 × 50 mm in size, accurate within 0.1 mm, and with a density as close to the theoretical as possible.

These briquets could be turned out by diamond grinding wheels, starting with the sintered products secured under the conditions described above. Their mean density exceeded 2.90. Their purity was equivalent to an absorption of thermal neutrons lower than that due to 1800 ppm of iron in the beryllium oxide.

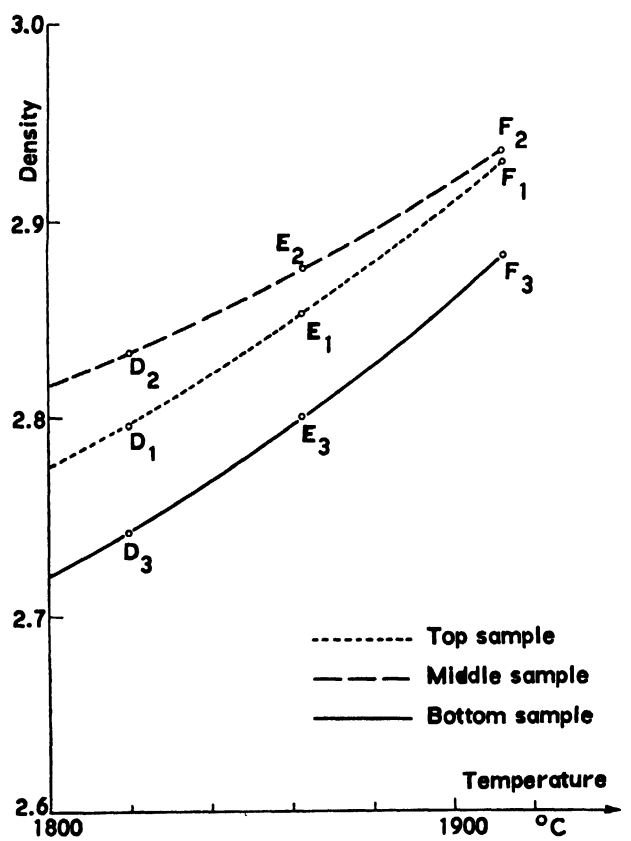

Figure 11. Distribution of density inside a briquet

The briquets contain a small percentage of graphite that is always less than 1%, largely introduced at the very outset of the sintering process, when the powder is packed into the mold by the progressive descent of the piston. This low percentage of graphite is unobjectionable in the proposed use of the briquets.

CONCLUSION

During the development of this process several observations were made which may be useful in interpreting the phenomenon of sintering.

Sintering under pressure evinces the influence upon the compacting kinetics of a force that produces the plastic flow of the material. We see that all the residual porosity is sealed off when compacting is highly advanced.

Mackenzie and Shuttleworth,[3] as well as other authors,[4] have suggested action analogous to that of surface tension as a basic hypothesis to interpret the phenomenon of sintering. Murray followed a parallel course[2] in pressure sintering.

These interpretations, however, make no allowance for the recrystallizations and orientations, important though they are, produced by the application of pressure during heating. Schemes analogous to those advanced by Kingston, Hüttig, and Hausner[5] might do so, perhaps.

We believe that it is necessary, before all else, to clear up more thoroughly the relationships between experimental results and sintering conditions. We have already noted the influence of the dimensions of the sintered product upon the results obtained. Moreover, our experiments in industrial fabrication indicate the consequences, important at times, of a slight deviation in particle-size distribution or chemical composition.

It is not impossible that appreciable discrepancies may appear between experimental observations that are analogous in principle, due to the absence or the presence of traces of impurities.

Therefore, we regard the foregoing results, aside from their practical application, merely as general indications of the progress of sintering under pressure.

In our opinion, quantitative comprehension of this phenomenon would require very extensive research, involving the procurement of raw material as pure and as physically definite as possible.

This research on beryllium oxide has been done within the framework of atomic cooperation between India and France.

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Purification of Beryllium Oxide

By A. E. Cairo and M. B. Crespi,* Argentina

The purification of beryllium oxide offers considerable interest from the nuclear standpoint, in view of its potentialities in the atomic field.[1]

The laboratory methods in use[2] customarily rest on the basic beryllium acetate solubility in organic solvents, particularly chloroform, in which its solubility is 33% at 18°C.[3] The specificity of beryllium regarding the formation of this compound makes it possible to achieve a high degree of purification.

In its most usual form, the method consists of transforming basic hydroxide or carbonate of beryllium into basic acetates by repeated evaporation with acetic acid, and thereafter to dissolve this compound in chloroform. The basic acetate is recovered by evaporation of the solvent, which thereafter gives the purified oxide by a new transformation in which it is still more highly purified.[4, 5]

The method mentioned presents various drawbacks. In the first place, in order for the transformation into basic acetate to be complete, it is necessary to carry out at least two evaporations with acetic acid, and, in these evaporations, the temperature must be controlled carefully in order to rule out volatilization of a part of the basic acetate. According to Kleinberg and his group,[2] 330°C must not be exceeded, which is the accepted boiling point for the basic acetate[6, 7] while, according to Besson and Hardt,[3] volatilization already begins at 230°C. We found, none the less, by using radioactive beryllium, that, by heating in an open vessel at 150 to 170°C, the vapors already show radioactivity and give a positive reaction for beryllium with quinalizarine when condensed. In view of the high toxicity of beryllium, the tolerance dose of which is 1 microgram per cubic meter,[8] it is important to allow for this fact. On the other hand, the degree of purification is poor with respect to some elements. Zinc also gives a basic acetate, which is soluble in chloroform,[9] and a similar salt has been described for zirconium.[10]

For these reasons, we thought that it would be appropriate to carry out purification in the liquid phase, and the preliminary work was directed at the production of a basic acetate in a phase made up of acetic acid and chloroform, after which the impurities would be extracted with water. Beryllium also is extracted, and hydrolizes according to the formula:

$$(AcO)_6Be_4O + 2H_2O \rightarrow (AcO)2Be_4O_3 + 4AcOH$$

However, the hydrolysis is slow.[11] The method was preceded by that described in ref. 12. Thereafter, acetic anhydride was used instead of the acid, in order to obtain more concentrated solutions, a substance the use of which for the formation of basic acetates has been recommended by Spaeth[13] and used by Guinet[11] and Kawecki.[14]

As a starting point for the purification tests, basic beryllium carbonate was chosen, since it is a substance which is more readily precipitated and filtered than the hydroxide. The basic carbonate is not a well defined chemical species, rather a mixture of carbonate, hydroxide, and water,[15, 16] and its formula depends on the precipitation conditions (concentration of the salts used, temperature, etc.),[17] which must first be tested out.

Once a satisfactory method has been established from the standpoint of the beryllium yield, a study was initiated, using radioisotopes, of the degree of purification which can be achieved with it. This work continues.

EXPERIMENTAL PART

Definition of the Method

In view of the variability of its formula, various conditions were tested for the precipitation of the basic carbonate. On the basis of the results obtained in dissolving experiments with the various precipitates, the following method finally was adopted: The beryllium solution, containing 3–4% of beryllium sulfate, is brought up to 12–13% in ammonium carbonate and heated with agitation, until it is brought to a slow boil. The precipitate formed disappears when stirred, and thereafter precipitates a

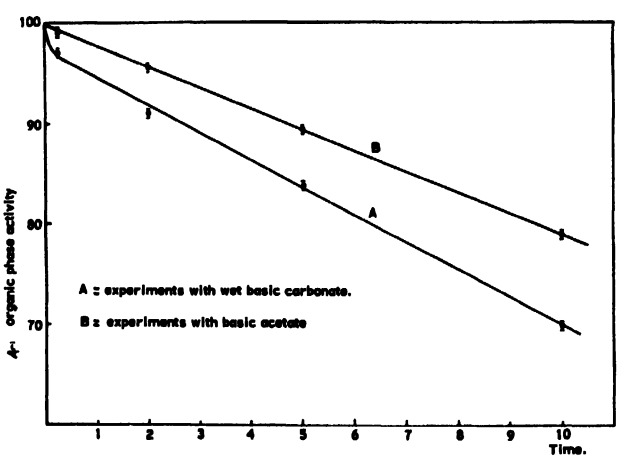

Figure 1

Original language: Spanish.

* Comisión Nacional de la Energía Atómica, Argentina.

Table I. Per Cent Activity in the Organic Phase as a Function of the Stirring Time*

System: 220 mg of wet basic carbonate + 1.01 ml of Ac_2O + 9.7 ml $CHCl_3$; extracted with 9.3 ml of water.
Starting concentration of beryllium in the organic phase: 2% expressed as basic acetate.

time	Activity
0	100
15 sec	98
5 min	96.5
10	95.5
15	93.5
25	91.0
40	86.5
64	80.0
124	68.0

* Average of three experiments.

Table II. Per Cent Activity in the Organic Phase as a Function of the Stirring Time*

System A: 700 mg of wet basic carbonate + 3.17 gm acetic anhydride + 3.5 ml chloroform; extracted with 14 ml of water.
System B: 682 mg of basic acetate + 3.12 gm acetic acid + 3.5 ml chloroform; extracted with 14 ml of water.
Initial concentration of beryllium in the organic phase, in both instances: 10%, expressed as basic acetate.

	Activity of system	
Time	A	B
0	100	100
15 sec	97.0	99.0
2 min	91.0	95.5
5	84.0	89.5
10	70.0	79.0

* Average of three experiments.

compound which readily forms a sediment. This is filtered and compressed to approximately 2 atmospheres, in order to eliminate the major part of the mother liquors. The formula, after washing and drying at constant weight on sulfuric acid, corresponds to approximately 40% BeO, 15% CO_2 and 45% H_2O, and conforms with a similar precipitate described in.[17] No appreciable differences were observed in composition or behavior, between those obtained at various times.

In the experiments, the basic carbonate was used without drying, after pressing. This left some 40% of mother liquors.

In the cases in which Be^7 was used as a radioactive tracer, it was added in a soluble form to the starting solution of beryllium, and precipitated by the same technique, in the form of basic carbonate, tagged by Be^7.

The basic carbonate so obtained was dissolved, and heated under reflux in a mixture of chloroform and acetic anhydride. The quantity of acetic anhydride was computed in each case, in agreement with the analysis of the wet product, in order that the reaction:

$$n(CO_2)\ m\mathrm{BeO}\cdot x\mathrm{H_2O} + [(\tfrac{3}{4}m + x]\mathrm{Ac_2O} \rightarrow n\mathrm{CO_2} + m/4(\mathrm{AcO})_6\mathrm{Be_4O} + 2x\mathrm{AcOH}$$

take place stoichiometrically.

The system obtained in those conditions is homogeneous at room temperature (18–20°C) for concentrations of some 2–3% measured in basic beryllium acetate. At the higher concentrations (work was carried out to concentrations of up to 10% of basic acetate), the compound becomes turbid, but the turbidity disappears when working at 30 to 35°C, which offers no difficulty.

The organic solution was extracted with water, and the phases were separated following a short period of agitation. The major part of the beryllium remained in the organic phase and the impurities, with the excess of acetic acid, in the aqueous phase.

The beryllium yield of the operation depends on the agitation time. In order to study it, experiments were carried out, using basic beryllium carbonate tagged with Be^7, and measuring the gamma activity of both phases, after they had been separated, as a function of the agitation or stirring time. Table I is the result for a starting beryllium concentration, in the organic phase, of approximately 2% in basic acetate; Table II for 10% of the same substance. In the case of Table II, the organic phase retained after stirring, a concentration of 17% of basic acetate.

On the same Table II, we show the results obtained with Be^7 tagged basic beryllium acetate purified by two crystalizations in acetic acid. To the chloroform solution of the latter, we added acetic acid in such a dose that the system so formed (B) would remain identical to that obtained with the method studied (A) if basic acetate had been formed in it with the whole of the beryllium. The results, for both systems, can also be seen on Fig. 1.

Radioactivity measurements were carried out, in every instance, with a statistical error of the order of 0.5%, giving an error limit of 1% for the values shown on Tables I and II.

Yield or Efficiency of Evaporation Method

A measurement of the efficiency of the conventional method was made, using beryllium carbonate which had been tagged with Be^7, and evaporating twice with acetic acid. In the screening experiments, it was shown that the temperature must not exceed 150 to 170°C. At this temperature, there begins to be some activity in the vapors.

We worked with a total activity of 3887 ± 38 cpm and recovered, by evaporation of the solution, 3770 ± 33 cpm. Thus, the efficiency of the operation is 3770/3887 = 97 ± 2% in beryllium recovered.

Table III. Separation Factor Obtained

Impurity	Activity of aqueous phase	Activity of organic phase	Purification
^{65}Zn	4422 ± 31	7 ± 2	650
$^{204}Tl^3$	1725 ± 16	13 ± 2	134
$^{51}Cr^3$	4942 ± 40	45 ± 4	124
$^{141}Ce^3$	4990 ± 35	52 ± 4	116

Elimination of Impurities

Various radioactive isotopes were added to the organic phase in a soluble form, and their distribution, in both phases, was determined after 15 seconds of stirring.

The experiments conducted until now are condensed in Table III. In that table, purification is expressed as follows:

$$\frac{\text{activity of aqueous phase} + \text{activity of organic phase}}{\text{activity of organic phase}}$$

CONCLUSIONS

The results obtained until now indicate that the percentage of beryllium which remains in the organic phase is sufficient for the purposes pursued, both in the 2% solution and in the 10% solution, provided the stirring or agitation time be not unduly long. In Tables I and II and curve *A* of Fig. 1, it can be seen that it is possible to extract the 2–3% solution for 10 minutes, and the 10% solution for 1 minute without having the efficiency drop under 95%. This time is sufficient to reduce the initial content of the impurities dealt with to less than 1%, until the present time, shown on Table III.

Figure 1 also suggests that, when dissolving, not all the Be is transformed into basic acetate having formula $(AcO)_6Be_4O$. The curve obtained by extracting this substance (curve *B*) goes down steadily from the 100% point: that which corresponds to the method under study, on the other hand, has a sudden jump to 97%, and thereafter continues like the other one, although it has a somewhat sharper slope. This behavior would have to be expected if the formation of basic acetate were incomplete, leaving 3% of the Be in a form rapidly extractable with water. A possibility is the formation of $(AcO)_2Be_4O_3$, mentioned in reference 11.

We consider it worthwhile to publish these first results, although the applicability of the method will be determined only when they would have been complemented, for other possible impurities, by a study of the degree of purification which can be reached in such cases.

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Production of Pure Beryllium Oxide

By J. C. Hutter and L. Pingard,* France

Most of the industrial processes used today for treating beryllium ores with a view to obtaining either alloys or the pure metal, which are the principal uses of this substance, use beryllium oxide as an intermediate. Beryllium oxide itself has some applications as a refractory and is used as raw material for the production of various beryllium compounds.

Beryllium oxide has been manufactured industrially for a long time. In France the Péchiney Company, which has been producing it together with other beryllium derivatives since 1933, was asked by the Commissariat à l'énergie Atomique to investigate and perfect industrial manufacture of the pure oxide, containing more than 99.95% of BeO, for nuclear applications. Thanks to the experience it had in this field, it was able to satisfy the Commissariat's request, enabling it to realize is program for the use of sintered beryllium on schedule.

Although the manufacture of beryllium oxide does not present very great difficulties when the problem involves obtaining a product of commercial purity the problems are much more complicated when very high purity is required. Not only must a correct process be used, but it must be conducted under such conditions that all the operations are protected from any possible contamination.

In the present case it was essential that the total impurities content, after sintering in brick form, should be below 500 ppm, and some of these impurities should be present in amounts less than 0.5 ppm, such as boron, cadmium, lithium, etc.

The first problem was therefore to perfect analytical methods making it possible to follow up the operations and evaluate the effectiveness of the proposed treatments. Then, after studying the various processes, we had to choose one that could be carried out industrially in a very short time and with materials that would not introduce undesirable contamination. Intensive study of the materials had to be made, therefore. Erection of the plant was further complicated by the precautions required because of the toxic nature of beryllium compounds.

VARIOUS PREPARATIONS OF BERYLLIUM OXIDE

Raw Materials

Although beryllium-containing minerals are largely distributed in nature (0.001% of the earth's crust), they are usually present in relatively small masses, and as a rule their production is subsidiary to the extraction of more important minerals with which they are associated (feldspar, asbestos, mica, etc.)

In actual industrial practice, the only mineral to be treated is beryl, with the formula $6SiO_2 \cdot Al_2O_3 \cdot 3BeO$, whose commercial composition varies as follows: BeO 11 to 13%; Al_2O_3 17 to 19%; SiO_2 64 to 70%; alkaline oxides 1 to 2%; and iron and other oxides 1 to 2%.

The most important deposits of this ore are in India, South America, (especially in Brazil), Madagascar, Morocco and Portugal.

The other minerals containing beryllium are much rarer: three of them might possibly be considered as sources of beryllium: chrysoberyl ($Al_2O_3 \cdot BeO$)–phenacite (SiO_2, $2BeO$) and helvite (a complex silicate).

The annual world production of beryl is certainly not more than ten thousand tons.

Beryl has a hardness of 7.5 to 8 (Mohs scale), and a density of 2.6 to 2.8: when crushed, it's apparent density varies according to the degree of crushing, from 1.5 to 2.

Review of Industrial Treatment Processes

We shall only give a rapid sketch of the industrial processes using beryl as a raw material. Most of these processes stem from Lebeau's work on the chemistry of beryllium.[1]

Preliminary Alkaline Digestion, followed by Dissolution by means of an Acid

In this process, the beryl is prepared for reaction by preliminary fusion or sintering with a caustic alkali or an alkaline carbonate or lime. The reaction product is then taken up by an acid, usually sulfuric acid, rendering the silica insoluble.

The alumina is eliminated in the form of ammonium alum, and the iron and the remaining impurities are eliminated by precipitation at controlled pH, after oxidation by means of an alkali or calcium carbonate. Finally, the beryllium hydroxide is precipitated by soda or ammonia.

Among these processes the following may be mentioned:

1. The Degussa process,[2] also used by the Beryllium Corporation; in this process, in which the beryl is melted with lime before the sulfuric acid digestion; the solutions are purified as above, the ammonia used in the final precipitation being recovered by causticization with lime.

Original language: French.
* Société Péchiney.

2. The Joy-Windecker process,[3,4] which employs preliminary fusion with sodium carbonate, followed by sulfuric acid digestion and purification by means of sodium carbonate. The impure beryllium hydroxide precipitated is redissolved and reprecipitated after purification by adjusting the pH to 5.5–5.7 with ammonia; the final precipitation is also made with ammonia.

3. The St. Gobain process,[5] in which the beryl is sintered with sodium carbonate between 900–1000°, and the frit treated with strong acids; the dissolved oxides are then reprecipitated with sodium carbonate and redissolved with molten caustic soda, which leaves the beryllium, iron and titanium oxides insoluble.

After these insoluble products are redissolved, the solution obtained is purified under controlled pH, using the zinc ferrocyanide process, especially for elimination of the iron. The beryllium hydroxide is then precipitated.

4. The McKee process,[5] in which the beryl is reacted with soda in an autoclave at 180°, or with molten soda, being converted into a silicoaluminate and a silicoberyllate. The beryllium is then brought into solution by means of sodium bicarbonate.

Acid Digestion after Preliminary Fusion of the Beryl

Sawyer-Kjellgren process,[7,8] used by the Brush Beryllium Co., consisting of making the beryl susceptible to reaction by melting it at 1625° and plunging it in cold water. After crushing, it is reacted with concentrated sulfuric acid, so as to insolubilize the silica. The aluminum is eliminated as ammonium alum, after which crude beryllium sulfate is crystallized, and then purified by redissolution in an ammonium sulfate solution. The beryllium sulfate obtained is calcined at 1300° in order to obtain pure beryllium oxide.

Reaction with Fluorine Compounds

Beryl is attacked between 700 and 1000° by fluorine compounds: sodium acid fluoride, ammonium acid fluoride, sodium fluosilicate or sodium fluoferrate forming sodium fluoberyllate, which is soluble in water, whereas the other impurities of the mineral remain insoluble.

These procedures include:

1. The Copaux-Kawecki process,[9,10] used by the Beryllium Corporation, employs sodium fluoferrate, which can be regenerated from the sodium fluoride solutions obtained after precipitation of the beryllium hydroxide. The Beryllium Corporation has likewise proposed attacking the beryl with a mixture of sodium fluosilicate and sodium fluoride.

Attacking the beryl with sodium fluosilicate alone was first proposed by Copaux[11] and then by Illig, Hosenfeld, and Fischer,[12] who reduced the amount of fluosillicate employed, while performing the reaction by sintering rather than by fusion. A process similar to this last one has been used by the Péchiney Company at Salindres since 1933.

It has likewise been proposed to prepare the fluoride, BeF_2, by reacting gaseous ammonium acid fluoride at 600° with pulverized beryl. This makes it possible to attack solely the BeO, and then return to the beryllium oxide by hydrolysis of the fluoride by superheated steam at 500°.

Reaction with Chlorine

In addition to these general processes, an endeavor has been made to perfect a method that would process the mineral directly into the chloride by a high-temperature reaction of chlorine with a previously sintered mixture of beryl and coal.

More recently, the Sheer-Kroman process[13] developed by the Light Metals Refining Corp., produces beryllium chloride directly by passing chlorine into an arc furnace whose electrodes are made of finely ground beryl, mixed with 30% of pulverized coal and agglomerated with a suitable blinder. The chlorides obtained are then separated.

METHOD OF PURIFYING THE HYDROXIDE

All the processes described above give a product that is not pure enough for atomic use.

However, the processes involving a fluorine reaction have the advantage of yielding oxides from which the impurities are easily eliminated; this is why we have retained this procedure and investigated the purification of a beryllium hydroxide that it yields.

There were various avenues of approach to this problem:

Distillation of Beryllium Chloride

This method is based on the differences in the condensation temperatures of the volatile chlorides. It is apparently simple, but very delicate to conduct on an industrial scale, largely because of the contaminations introduced by the materials used in constructing the apparatus and, again, because of the toxicity of beryllium compounds.

Sublimation or Extraction of Beryllium Basic Acetate by Chloroform

The action of acetic acid on beryllium hydroxide, nitrate, or chloride yields beryllium basic acetate,[14,15,16] with the formula: $[Be(CH_3CO_2)_2]_3BeO$. This melts at 238°C and boils at 330°C at atmospheric pressure. *In vacuo*, it begins to sublime at 95°C.[17]

It is soluble in chloroform to the extent of 33.3 gm of acetate per 100 gm of chloroform. Evaporation of the solution leaves crystals of beryllium basic acetate.

Thanks to these properties, beryllium can be separated from most elements, either by distillation or sublimation of the basic acetate, or by chloroform extraction. Our experiments have shown that only zinc acetate sublimed with beryllium basic acetate, and that only iron acetate is extracted by chloroform to any considerable extent. Manganic acetate, which

is soluble in chloroform, is easily decomposed by reduction in solution or by calcination at 200°.

Accordingly, distillation and chloroform extraction of beryllium basic acetate are powerful methods for purifying beryllium compounds. However, industrial operation is complicated by the same factors as in distillation of the chloride. Further, it is not easy to convert the basic acetate into the oxide. We therefore abandoned industrial application of this process, but still employ it in the laboratory for the preparation of standards (total content in impurities below 50 ppm).

Crystallization of Beryllium Salts

A standard purification method is crystallization. In the case of beryllium, this method is particularly applicable because of the great differences between hot and cold, neutral and acid, media, in the solubility of certain salts, such as the nitrate and the sulfate.

For the nitrate, $Be(NO_3)_2$ the solubility, which is 64% at 60°C drops to 52% at 20°C[18] and to 29% at 20°C in the presence of 50% of HNO_3.[19]

For the sulfate, $BeSO_4$ at 100°C, the solubility, which is 45% falls to 29% at 25°C, 12% at 25°C in the presence of 23% of H_2SO_4, and 0.9% at 25°C in the presence of 66% of H_2SO_4.[20]

Precipitation of a nitrate with 3 and 4 molecules of water, and of the sulphate with 4 molecules of water, increases the crystallization yield by decreasing the mother liquors.

Crystallization of the nitrate, which should be conducted in a medium rich in nitric acid, has the drawback of considerable evolution of nitrous fumes. We therefore preferred crystallization of the sulfate, which is the solution we finally adopted.

By itself, this crystallization is not enough to give a pure enough product with a good yield.

The excessive impurities, especially silica, contained by industrial beryllia, would require a double crystallization and the mother liquor would have too many impurities to be recycled without purification.

It was thus necessary to effect purification before crystallizing the sulfate; this is done by making the silica insoluble with sulfuric acid, precipitating the sulfide, and precipitating the ferric hydroxide pH 4.5.

PROCEDURE ADOPTED FOR PURIFYING THE BERYLLIA

The following operations are involved in the preparation of pure beryllia from the industrial beryllia obtained from beryl by the fluocilicate process:

Sulfuric Acid Treatment

The hydrated technical beryllia is reacted with sulfuric acid diluted with the mother liquor of the beryllium sulfate crystallization. In a concentrated $BeSO_4$ medium (about 400 gm/l), the silica is rendered insoluble by heating to 105°C in the presence of a few grams of free acid per liter, and it is not necessary to evaporate dry.

If the fluorine content of the beryllia is too high, some of the silica distils over as fluosilicic acid, but part remains in solution in the same state. This causes no trouble, since the fluosilicic acid will remain in solution when the beryllium sulfate crystallizes out.

Dilution and Precipitation of Sulfides

The sulfuric acid solution is diluted with the wash waters of the beryllium sulfate and water, in order to bring the concentration to about 35 gm of BeO per liter, and is then separated with hydrogen sulfide.

Filtration of Silica and Sulfides

The sulfide precipitate coats the silica and makes it possible to decant and filter it.

Precipitation of Iron

The excess H_2S is removed from the filtered solution by bubbling in air, and the solution is then oxidized by bubbling chlorine through it. The ferric hydroxide is precipitated by bubbling with ammonia to pH 4.5. A portion of the alumina precipitates with the ferric hydroxide.

Filtration of the Hydroxides Precipitation of Beryllium Hydroxide

A beryllium hydroxide, of medium purity, is precipitated by bubbling ammonia through it. The purpose of this operation is to eliminate certain impurities: Ca, Mg, Cu, Na, etc., and to enable us to prepare a concentrated solution of sulfate without evaporation.

Filtration of Beryllium Hydroxide Dissolution in Sulfuric Acid

The wet hydrated beryllium hydrate is dissolved in the equivalent amount of 98% acid, and the solution is concentrated until its boiling point is 110°.

Crystallization

98% sulfuric acid is added so as to bring the acid concentration to 20 gm/l, and it is allowed to cool with stirring. Crystals from a prior operation are added in order to obtain regular crystallization.

Drying the Crystals

The mother liquor is recycled to react with the technical beryllium hydroxide, and the wash waters are used to dilute the sulfuric acid solution.

Dissolution of Beryllium Sulfate and Precipitation of Beryllium Hydroxide

The crystals are dissolved in water, and the solution filtered. The beryllium hydroxide is precipitated by bubbling with ammonia.

This beryllium hydroxide precipitation, like the first one, should be conducted in such conditions that a dense and filterable precipitate is obtained.

Special study was required for perfecting this precipitation, for beryllium hydroxide has an unfortunate tendency to precipitate as a very absorbent gel that is difficult or impossible to wash.

Filtration of Beryllium Hydroxide

It is vacuum filtered and washed with water.

Drying and Calcination

These operations preparatory to sintering do not present any particular difficulties, except the precautions to prevent contamination on the one hand, and the dangers of leakage, on the other.

Beryllium hydroxide, in point of fact, is probably the most dangerous compound from the point of view of toxicity, and the greatest care should be taken in handling it once it is in the dry state.

In particular, the beryllium hydroxide must be agglomerated upon leaving the filter, before it undergoes the drying and calcination operations.

Results

Starting with technical beryllium hydroxide containing 98% BeO and a great number of impurities: F, Na, Si, Fe, Mn, Al, etc., after calcination around 1000°C, this process enabled us to obtain beryllium oxide more than 99.95% pure, containing less than 100 ppm, of Fe, less than 100 ppm of Si, about 100 ppm of Al and less than 0.3 ppm of B.

INDUSTRIAL PRODUCTION

All the operations employed in the process that has just been described are simple and standard procedures of the chemical industry. But whereas a sheet-iron or wooden vat would have been adequate usually, we had to make use of special materials in order to avoid any contamination. There is no point to carrying out a chemical purification process if the materials in which the reactions are performed themselves introduce impurities. Contents of the order of 1 ppm can easily be introduced by the mere contact of a solution with a material containing the elements in question.

We therefore made a systematic study of the materials that could be employed for the various operations: ebonite and rubber, enamels, Isolemail, plastics, wood, etc.

Qualitative spectrographic analysis of these various materials enabled us at the outset to eliminate any that contained appreciable amounts of the most troublesome elements.

We then determined those impurities in the materials that could pass into solution either in a sulfuric acid or in an ammonia medium, under the conditions of the process, using spectrographic examination of dry extracts of solutions that had been in contact with them for a long time. We eliminated those materials that allowed too large an amount of impurities to pass.

Finally, we studied the resistance of the materials that had given satisfactory results in the two preceding tests, under the specific conditions of the various operations.

As a result of these tests, we decided on the following materials: sulfuric acid reaction—lead-lined tank (chemical lead); hydroxide precipitation—ebonite-lined tank (special ebonite composition); dissolution and crystallization of the sulfate—tank enameled with a special boron-free enamel, using a steam jacket; and wooden filters coated with polyvinyl chloride.

All the tubing is of polyvinyl chloride. In order to prevent contamination with dust, all the apparatus (filters, tanks, etc.) are closed.

All the water used in the laboratory is softened in a three-element ion exchanger: cations; anions; Si and B. After demineralization, the boron content is of the order of one microgram per liter, as against 100 in natural water and 10–20 in distilled water.

Because of the toxic nature of beryllium compounds, the fumes, vapors, and dust are collected from all the apparatus in a cleaning system. The evacuated air is then freed of dust by filtration and washing before being directed to the chimney stack.

ANALYTICAL CONTROL

Methods must be available for determining traces in order to perfect the purifying process and, later, to control manufacture. At first we made these determinations by colorimetric methods. However, in view of the large number of samples to be analyzed and the great number of elements to be determined in each sample, we were led to employ quantitative spectrography. The fact is that since most of the elements are more or less troublesome, we would have needed an entire analytical chemistry laboratory specializing in trace determination to make these analyses.

Only spectrography could provide enough results within a reasonable time. A simple and rapid technique had to be found, at the expense of precision if necessary. For a relative error of 20% is unimportant when the content is of the order of a few parts per million.

Analysis at all the stages of manufacture was reduced to analysis of the oxide, BeO.

Since beryllium oxide is refractory and not a conductor, the only source that could be used was the electric arc. We chose the direct-current arc furnished by a 220-volt generator. Although it is possible to obtain greater precision and, for certain elements (Al), greater sensitivity by mixing the beryllium oxide with graphite, barium oxide and an internal standard (tin in the form of SnO_2),[21] we preferred to use beryllium oxide itself, without any addition in our spectram analysis. This gives a relatively stable arc and, if the same operating conditions are always maintained, the reproducibility is satisfactory. The sensitivity is greater for the most deleterious elements (B, Cd, Li). This sensitivity could be increased by employing a high current (10 amp) and by grooving the lower electrode below the crater in such a way as to concentrate the heat there. Under these conditions, the beryllium oxide charge melts completely.

For the refractory elements, or those whose oxides are refractory which are greatly influenced

by graphite, the content is given by the ratio of the intensities of their lines to the weak lines of beryllium:

$$\frac{\text{Al } 3082}{\text{Be } 3111}\ \frac{\text{Mg } 2852}{\text{Be } 2898}\ \frac{\text{Si } 2881}{\text{Be } 2898}\ \text{etc.}$$

We have proved that these ratios remain constant for a given content, despite great variations in the absolute intensities of the lines, and it is confirmed by the large number of analyses already made which require spectrography of the same standards a large number of times.

For elements that are easily volatilized in the arc, the content is given by the ratio of the intensity of their lines to that of the continuous background: Cu 3274, Fe 2599, B 2497, Cd 2288, Li 6701, etc. For the spectrum range 2000–5000Å, we used the Q24 Zeiss spectrograph with Guilleminot Spectroguil plates, and for the alkalies, the Huet UV 30 Spectrograph, with a spectral range extending up to 10,000 Å, with Gevaert plates that are sensitive to the near infrared.

The electrodes are Péchiney (Chedde) electrodes.

Under these conditions, the sensitivity limits are as follows: B 0.3 ppm; Cd 0.5; Li 1; Na 10; K 10; Cu 1; Mg 1; Mn 1; Fe 5; Si 10; Al 50.

The observed deviations are of the order of 10% at about 100 ppm and 30% for boron contents below 1 ppm.

Synthetic standards prepared on the basis of beryllium basic acetate extracted with chloroform and sublimed were used in calibration.

CONCLUSION AND SUMMARY

The intensive cooperation of the Commissariat à l'Energie Atomique and the Péchiney Co. enabled the latter to carry out its program for utilizing beryllium oxide.

Production on the industrial scale of beryllium oxide that was sufficiently pure, was made possible by studying the chemical purification of the technical hydroxide, by investigating the construction materials in order to avoid the dangers of contamination and by employing strict control, using quantitative spectrographic analysis at every stage of manufacture.

This work was done within the framework of atomic collaboration between India and France.

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The Spectrographic Determination of Microquantities of Beryllium and Its Application to Measurements in the Air and Organic Tissue

By A. G. Taudien,* Argentina

A method for the measurement of minute amounts of beryllium became needed because of its toxicity. Several spectroscopic methods have been proposed. Cholak[1] used the cathodic layer method. Barnes *et al.*,[2] and Peterson,[3] used the conventional direct current arc method; Smith *et al.*,[4] a set of rotatory electrodes with spark. Owen *et al.*[5] used the spark with porous graphite electrodes. Churchill and Gillieson[6] have recently designed a direct-reading instrument for continuous control of the beryllium in the air.

The need for monitoring air pollution in laboratories where beryllium compounds are investigated led us to a study of the spectrographic measurement of microquantities of this element. In our experiments, we used a copper spark, because of its high sensitivity and reproducibility, as well as the ease of the procedure. This paper describes our preliminary results.

A Model E 492 of the Hilger high-dispersion spectrograph with a quartz prism was used. The exciting source was a Hilger condensed spark, 15,000 volts; capacity, 0.005 mf; inductance, 0.13 mH. Photometry was done with a Model A N° K15 Kipp & Zonen recording microphotometer.

In the spectrographic procedure, we used a wavelength range of 2500–3000 Å, and an optical system consisting of condensing lens of $F_D = 65$ mm and a concave mirror. The slit was 20 microns-Ilford ordinary and Kodak SA_2 plates. The spark gap was 4 mm, and exposure 45 seconds. Kodak developer D-19, 3 minutes at 20°C, and Kodak fixer F-5, 10 minutes at 20°C were employed. 0.1 ml of the solution was deposited on two J. and Mathey "Spec-pure" copper electrodes 5 mm in diameter. Evaporation was done under infra-red lamp and the spectrum is produced.

As a test of sensitivity, we used the Be 3130.4 and 3131.1 lines from 1 mγ of beryllium in an approximately decinormal HCl solution (one part conc. HCl in 99 parts H_2O) and (0.5 mγ in H_2SO_4 0.001*N*). No tests were made with lower concentrations than these but the density obtained (0.21) on SA_2 Kodak plates indicates the possibility of revealing the presence of 0.2 to 0.3 mγ of beryllium in the electrode.

The possibility of obtaining beryllium in sulfuric solution by the treatment of the sample led us to a study of the effect of sulfuric acidity on the intensity of the lines. Spectra were obtained by using 10 mγ Be in several acid concentrations. Table I gives the results.

There is a marked decrease in background and increase in the intensity of the Be 3130.4 line when acidity is reduced. This may be seen also on Fig. 1.

Where densities of the spectral lines of the solutions H_2SO_4, 0.001*N* and HCl, 0.1*N* are compared. The latter acidity is generally used with the copper spark method.

The possibility of precipitating Be from its solutions by using aluminum as a carrier to concentrate and separate this Be from the elements that may interfere, led us to a study of the influence of aluminum on the spectrographic determination. The results obtained, working with 10 mγ Be and variable concentrations of Al are shown on Fig. 2.

It was observed that, when Al is in a 100/1 ratio to Be, the density of the line decreases. In this method, addition of Al was not considered. However, this may be done if future tests indicate that the drop in sensitivity is compensated by Be concentration in a smaller volume.

Concentration curves were drawn for solutions: (i) from 0.5 mγ to 100 mγ Be in H_2SO_4 0.001*N* (Figs. 3a and 3b); (ii) from 1 to 20 mγ of Be in HCl 0.1*N* (Fig. 4).

Molybdenum, in the form of ammonium molybdate solution was added as internal standard, at the rate of 5 gammas Mo per ml.

Visual comparison with standard plates was made for concentrations higher than any of those shown on the curves.

Air samples of 10 m^3 volume were filtered through paper by suitable means. In a series of tests, the filter paper was attacked by H_2SO_4 and HNO_3 and the destruction was completed with $HClO_4$. The residue was dissolved in 0.5 ml concentrated HCl and H_2O.

In another series of tests, the filter paper and its contents were calcinated, the ashes were treated with H_2SO_4, the excess was eliminated by heating and the resulting salts dissolved with 0.5 ml conc. HCl and H_2O.

In both cases, the volume of the solution was com-

Original language: Spanish.

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Table I. Densities*

	Be 3131.4	Background	Cu 3128.7
H_2SO_4 0.001 *N* sol.	1.24	0.06	0.25
HCl 0.1 *N* sol.	0.96	0.18	1.09

* With 20 mγ Be on the electrodes.

pleted to 50 ml. The final acidity was adjusted with 0.1*N* HCl. To obtain the spectrum, 0.1 ml of this solution was evaporated on the copper electrode.

The results indicated that: (i) losses in Be occurred in the samples obtained by calcination; (ii) Be contamination was observed on the blank. Since it was higher for the sample obtained by sulfuric treatment, it must have originated in the glassware and not in the copper electrode. The use of new glass material was recommended; and (iii) the amount of Be found in the air samples was of a magnitude of 0.2 gammas per 1 m^3.

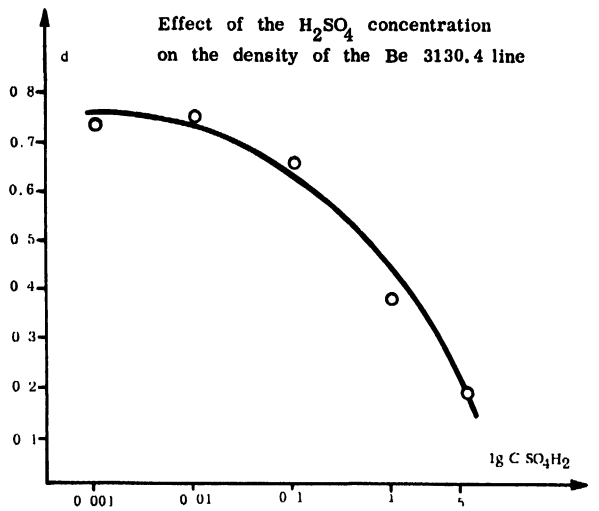

Figure 1. Effect of the H_2SO_4 concentration on the density of the Be 3130.4 line

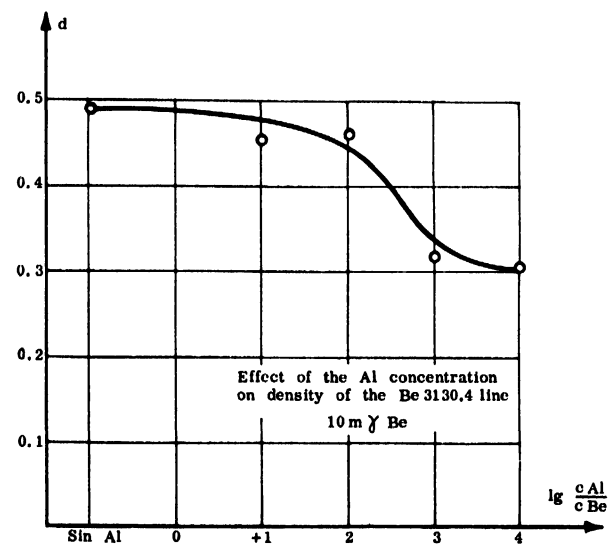

Figure 2. Effect of the Al concentration on the density of the Be 3130.4 line, 10 mγBe

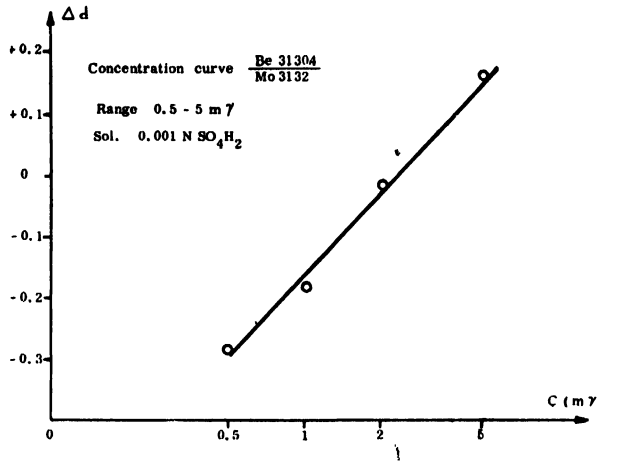

Figure 3a

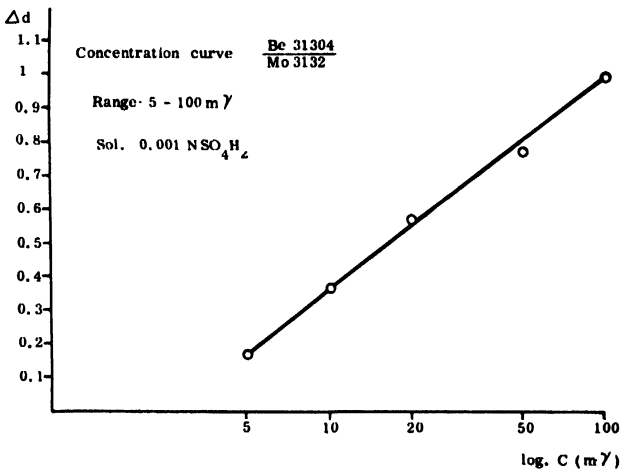

Figure 3b

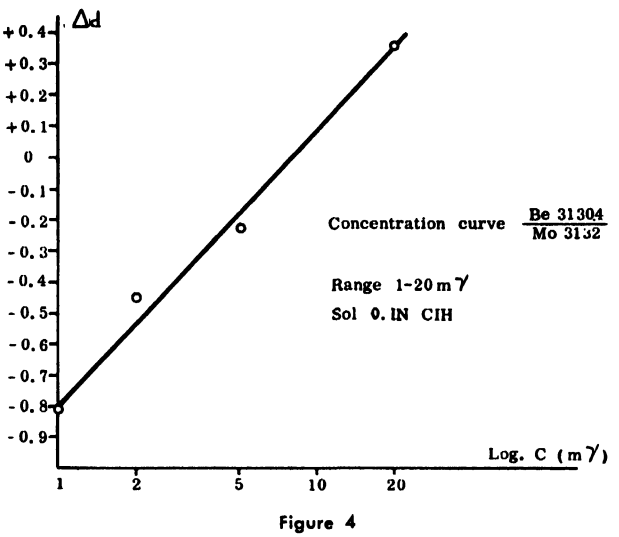

Figure 4

The method was applied to the study of Be in a solution prepared by the processing of lung tissue. The result was negative.

Since the solution contained appreciable amounts of Ca, Mg, and Na, that may lower the sensitivity, a recovery test was made adding Be to these ele-

ments at the rate of 50 mγ per ml (which is equivalent of 5 mγ in the electrode) a sensitivity considered to be sufficient. Two mγ were recovered. This was considered satisfactory for this problem.

CONCLUSION

It has been found that spectrographic determination of beryllium by the copper spark method is applicable to air and to biological tissue, and that for these applications made it possible to obtain high sensitivity.

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Enrichment of B^{10} in $B^{10}F_3$ by Thermal Diffusion

By Juan Alejandro McMillan,* Argentina

Watson, Buchanan and Elder[1] published an article in 1947, in which they described the successful enrichment of B^{10} in $B^{10}F_3$, in a Clusius type, hot wire apparatus of standard size. In 1952, Cooke and Mackenzie published, in a series on the properties of boron halides,[2] abundant information on the interactions between the molecules of BF_3. This paper gives a law on the variation of viscosity with the characteristic temperature of a Sutherlands molecule, i.e.:

$$\frac{\eta}{\eta_0} = \left[\frac{T_0 + S}{T + S}\right](T/T_0)^{3/2} \qquad (1)$$

giving also, for the constant, the value $S = 194.6°K$ which applies to the temperature intervals

$$293°K \leqslant T \leqslant 476°K$$

EXPERIMENTAL METHODS AND RESULTS

Since our purpose was the production of substancial qualities of BF_3 very enriched in B^{10}, we availed ourselves of Cooke and Mackenzie's results and decided to work with a temperature differential between the walls greater than the known applicability range of constant S. We assumed, other data being unavailable, that formula (I) would continue to be applicable, with the same value of S, even for a 293°K–673°K interval and, applying the Jones[3] expression of α for Sutherland's model with $\nu = 7$ (quantum model of the van der Waals forces),

$$\alpha = \frac{105}{118}\,\frac{m_2 - m_1}{m_2 + m_1}\,\frac{(1 - 0.98)(S/T)}{(1 + 0.92)(S/T)}$$

we obtained the following values

$\alpha \times 10^3$	t°C
0	−83
2.5	115
3.7	309
4.5	503

from which the deduction is warranted that at −83°C there is no separation while, at a lower temperature, the heavier molecules are concentrated on the hot zone. In the available work zone, however, the $B^{10}F_3$ molecule should concentrate on the hot wall and the effect should be all the greater as the temperature differential increases, always within the hypothesis of the validity of Equation 1.

Once the temperature interval 293–673°K is taken, giving T = 483°K for the mean temperature, the following mean values of the variables which determine the behavior of the gas during the thermal diffusion were obtained $\bar{\eta} = 250P$; $\bar{\rho} = 1.79$ gm/l; $\bar{\alpha} = 2.9 \times 2.9^{-3}$ (lineal approximation).

According to Chapman and Cowling,[4] the self diffusion factor is, in this case, as a first approximation

$$D = \frac{1.20\,\eta}{\rho[1 + (S/T)]}$$

and by substituting values we obtain

$$D = 0.12 \text{ cm}^2/\text{sec}$$

Using the Jones and Furry[5] nomenclature, the final table will be:

$\alpha = 2.9 \times 10^{-3}$	$T' = 673°K$
$\eta = 2.5 \times 10^{-4}$	$\overline{T} = 483°K$
$\rho = 1.8 \times 10^{-8}\,\rho$ gm-cm^{-3}	$T = 380°K$
$D = 0.12 \times$ cm^2 sec^{-1}	$T/\overline{T} = 0.79$
$T = 293°K$	$T' \cong 2T$

Using the Jones and Furry approximation for the case of a plane, and in order to obtain a sufficiently low Reynolds number, the separation between walls, $2w$ should be:

$$2w = \sqrt[6]{\frac{10!\,\eta^2 \cdot D^2 \cdot T^2}{g^2 \cdot \rho^2\,(\Delta T)^2}} = 0.34 \text{ cm}$$

Since this value insures a stabilized motion with a large safety margin, we decided to use an approximate value for a hot wire column, producing finally four thermal diffusion columns of 3 m each, in series, with 7 mm id tube and 0.3 mm nicrom wire, which gives an actual value of

$$2w = 3.35 \text{ mm}$$

The columns were connected in series with pairs of tubes of the same diameter, one of which was kept at 100°C over the whole of its length by means of an outside resistor.

The wire was kept under mechanical tension by means of a steel spring provided at the lower end, which we covered with mercury to avoid heating and ultimate destruction. Separators were placed at one meter intervals, made of nicrom wire coils of the same diameter. The wires were heated by direct current from a Cu_2O rectifier, the temperature being controlled by their degree of stretching. The installation was completely made of Pyrex glass and a mixture of equal parts of paraffin, and petrolatum was used for the vacuum valves, since it resists BF_3

Original language: Spanish.

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attack well. BF_3 from cylinders was used as a raw material.

A 15 day run was made with two equal containers at each end, loading the apparatus initially on BF_3 containing 18% B^{10}, at atmospheric pressure.

The B^{10} content of each container was determined after the run by the absorption of slow neutrons, measured by the activation of In foils. The 1.4 Mv Cockroft-Walton of this Commission was used, bombarding lithium with deuterons and slowing down the neutrons released, to thermal speed, through paraffin.

The results obtained were: 23% of B^{10} on the positive container and 13% B^{10} in the negative, leading to a value of the separation factor of

$$q = \frac{N' (1 - N'')}{N'' (1 - N')} = 2$$

corresponding to a separation factor, per meter, of:

$$q_0 = 1.06$$

with a production on the order of about 50 cm^3 of gas per cm^2 of column section per day.

Figuring, always following Jones and Furry, the q_0 theoretical value by the approximation

$$q = e^{H/K}$$

where

$$H = \frac{(2\pi\nu)^3 \rho^2 \alpha g B (\Delta T)^2}{6! \eta T^2}$$

$$K = K_c + K_d + K_p$$

$$K_c = \frac{(2\pi\nu)^7 \rho^3 g^2 B (\Delta T)^2}{9! \eta^2 \cdot D \cdot T^2}$$

$$K_d = \pi\nu\rho D \cdot B$$

$$K_p = k(K_c + K_d)$$

and giving K a value close to unity, as required by a wire eccentricity in the order of 10^{-1}, the theoretical value of q_0 is

$$(q_0)_t = 1.08$$

The difference is readily explained and due to the fact that the wire was excessively offset in one of the columns.

At the present time, having improved the construction of our installation, we replaced convexion for series coupling, by the use of single capillaries according to the Clusius method, and we are experimenting with alternating current.

After the completion of this article, Cooke, Hawes and Mackenzie[6] published an article describing their measurements with columns made of stainless steel concentric tubes. These measurements check very well with the model adopted by said authors.

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The Preparation of Borazol

By Gerardo J. Videla and Mauricio F. Bühler,* Argentina

The purpose of this preliminary paper is to submit some of the results obtained in the course of the preparation of borazol without any need for lithium borohydride.

This reagent has been used either as a source of boron in the method[1] based on the reaction:

$$3LiBH_4 + 3NH_4Cl = B_3N_3H_6 + 3LiCl + 9H_2 \quad (1)$$

or as a reducing agent in the method[2] using the reaction

$$B_3N_3H_3Cl_3 + 3LiBH_4 = B_3N_3H_6 + 3/2\ B_2H_6 + 3LiCl \quad (2)$$

Since the preparation of lithium borohydride is difficult, we have attempted to replace it by more readily obtainable raw materials. In the first case, a reaction was sought that would form it right *in situ* and that coupled with the Schaeffer, Schaeffer and Schlesinger reaction[1] would yield borazol; and, in the second, accepting the hypothesis that lithium borohydride is no more than a carrier of lithium hydride, it was felt that this latter substance should, under certain conditions, effect the reduction of trichloroborazol. Should this reaction happen in the absence of solvents, it would be possible, besides the advantage indicated, to avoid the simultaneous formation of diborane, the handling of which is troublesome, and to make easier the purification of the resulting borazol by making its separation in a solvent unnecessary.

It was proven qualitatively that, by heating lithium fluoborate to almost 200°C with a lithium hydride excess, it was possible to separate from the product of the reaction an ether soluble substance, the chemical behavior of which was that of a borohydride, while further heating of the mixture produced the release of diborane. Both reactions may be interpreted as follows:

$$LiBF_4 + 4LiH = LiBH_4 + 4LiF \quad (3)$$

$$2LiBH_4 = B_2H_6 + 2LiH \quad (4)$$

The formation of borohydride at a lower temperature than that necessary for the formation of borazol by the Schaeffer, Schaeffer and Schlesinger reaction[1] already mentioned made it possible to couple reaction 3 with reaction 1, that is to say:

$$3LiBF_4 + 12LiH + 3NH_4Cl = B_3N_3H_6 + 12LiF + 3LiCl + 9H_2$$

Using the same equipment, and working practically with the same conditions as did the authors mentioned above in the presence of an inert solvent, in order to increase the contact surface of the reagent, the first gross purification gave a yield of about 30% borazol of almost 95% purity.

On the other hand, the preliminary attempts at a reduction of trichloroborazol with lithium hydride, in the absence of solvents, led to the conclusion that, in order to obtain good results, the following are necessary:

(1) An activated lithium hydride offering great surface.

(2) Work at a temperature lower than that of decomposition for trichloroborazol.

(3) The rapid separation of the borazol formed from the reaction area.

These conditions are met rather well if the finely ground lithium hydride mixed with crushed Pyrex glass is activated by heating, if the reaction takes place at a temperature not higher than 180°C, and if the trichloroborazol is carried toward the reaction in a current of hydrogen which also makes it easier for the borazol formed to be carried away.

Working as mentioned above and duly regulating the rate of flow of the hydrogen-trichloroborazol mixture it is possible to recover, in the condensation trap, an impure borazol containing about 10% of chlorinated derivatives in a yield of from 60 to 70% of the theoretical maximum.

EXPERIMENTAL WORKS

The lithium hydride used was obtained from Metals & Chemicals Ltd., 16 Northumberland Ave., London W.C.2, in pieces, and contained 92–3% LiH. It was ground in a nitrogen atmosphere to a —200 mesh fineness. The activation of lithium hydride was done as follows: Place 12 grams lithium hydride (—200 mesh) mixed with 25 grams ground Pyrex glass in the horizontal oven (Fig. 1), previously cleaned with oxygen free nitrogen. Circulate hydrogen and heat the oven for a few minutes at 100°C. Cut the hydrogen flow and close stopcocks A and B, and raise the temperature to 300°C during two hours, stop heating and, opening stopcock A, cause hydrogen to pass during the cooling period.

Ammonium chloride of the purity required for analyses was used. It was dried at 180°C, and ground to a 200 mesh fineness.

Lithium fluoborate was prepared by neutralizing a fluoboric acid solution with lithium hydroxide, con-

Original language: Spanish.

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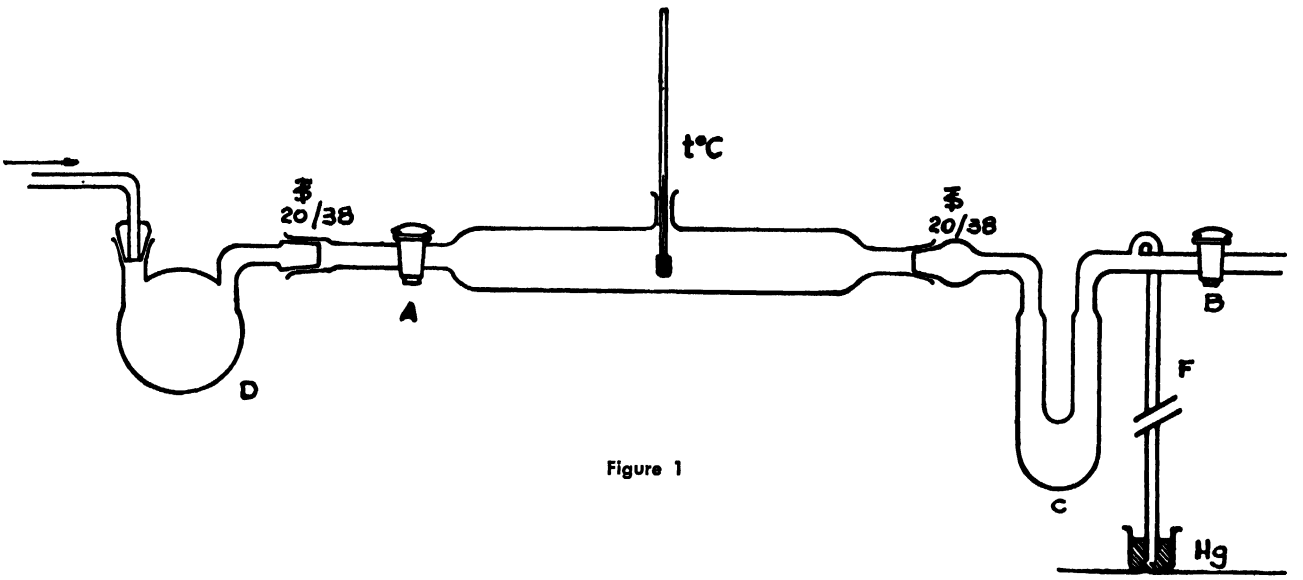

Figure 1

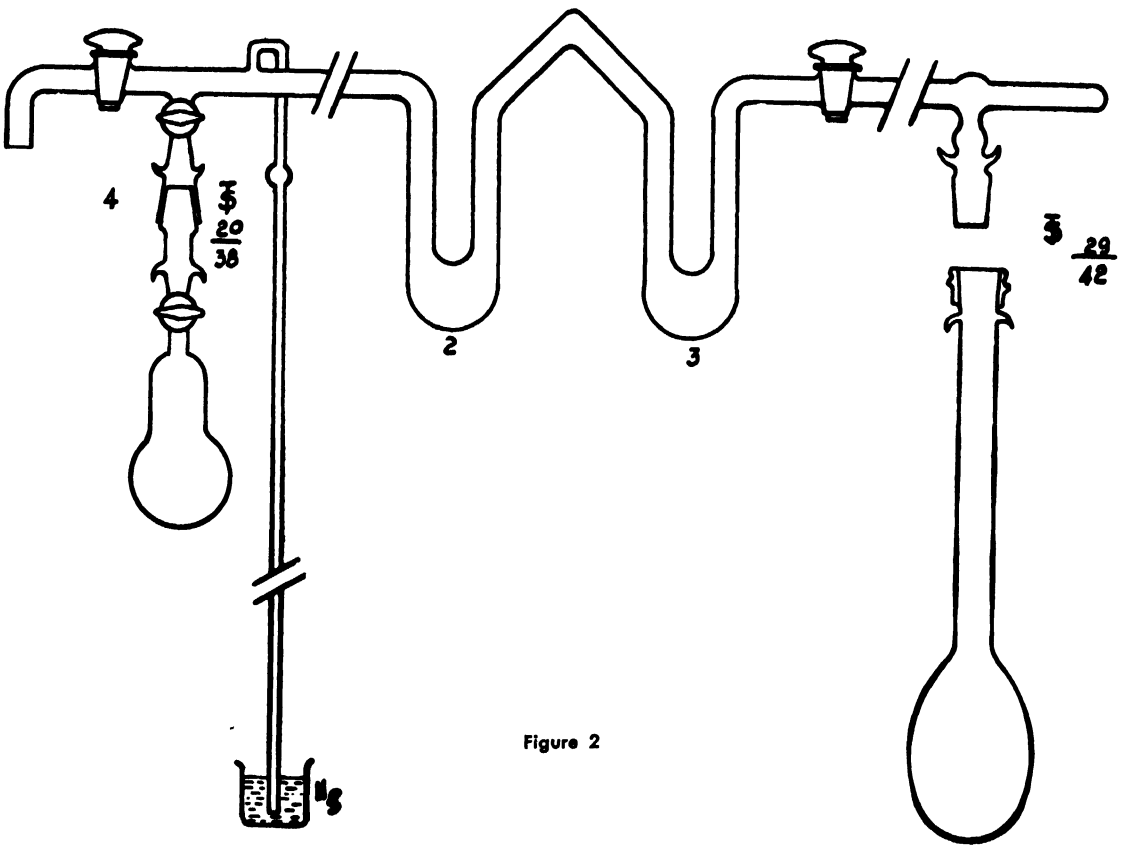

Figure 2

centrating the solution to dryness after filtration of some of the lithium chloride separated and eliminating boric acid traces by washing with alcohol. Finally, it was dried at 100°C under reduced pressure.

B-trichloroborazol was prepared following Heldberger's* process, which makes it easy to obtain it from ammonium chloride and boron trichloride, without any solvents. The impure product of the reaction is sublimated at lower pressures, at 100°C, producing 25–30% of the theoretical yield of pure B-trichloroborazol, beautifully crystallized.

Preparation of borazol by the reaction between lithium fluoborate, lithium hydride and ammonium chloride made use of the apparatus described by

*Johann Heinrich Heldberger, Comisión Nacional de la Energía Atómica; private communication.

Schaeffer, Schaeffer and Schlesinger,[1] illustrated in Fig. 2, and the work was done as indicated in the reference.

For the test, a mixture of 14.1 gm lithium fluoborate, 9.2 gm ammonium chloride and 4.8 gm lithium hydride with 25 gm crushed Pyrex glass was placed in the beaker. The latter was set up, vacuum was established, and traps 2 and 3 were submerged in liquid air. Operation was started heating first the neck of the beaker to 300°C, and thereafter raising its contents to 280–290°C until hydrogen release was started in the mercury bubbling tube, and then maintaining the temperature at 250–255°C. The hydrogen release stopped about two hours later. Heating was stopped and the equipment was carefully and slowly emptied. The material condensed in traps 2 and 3 was transferred through outlet 4 to a small beaker, and rectification under vacuum was done through a trap at —80°C. Between 60 and 65 ml of diborane were eliminated in this form, while there remained 1.15 gm (28.4%) impure borazol in the trap.

The product obtained has a melting point of about —60°C, and decomposes with release of hydrogen and reduces permanganate and nickel salts in an aqueous medium typical properties of borazol.[3]

Preparation of borazol by reduction of B–trichloroborazol with lithium hydride proceed as follows: Place 46 gm sublimated B–trichloroborazol in beaker D of apparatus shown in Fig. 1 and heat to 100°C while the reduction oven, loaded with 12 gm activated lithium hydride is maintained as previously described at 180°C; pass hydrogen at such a rate that the operation ends in about 40 or 50 minutes, and the condensable volatile products are recovered in trap C, cooled with liquid air. About 14 gm of the impure product are obtained, which, by the first fraction under vacuum through the —80°C bath, is freed from the greater part of the volatile impurities, but not from the chlorine derivatives which should be separated by more careful fraction.

The product thus obtained has a melting point of about —60°C, 76 mm vapor pressure at 0°C, and 85% distills between 50 and 60°C. Its analysis, as computed for $B_3N_3H_6$, B, 40.7%; N, 51.9%, as obtained: B, 39.7%; N, 50.5%; Cl, 4%.

SUMMARY

A study was made of two techniques of borazol preparation, which eliminates the need of lithium borohydride.

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Record of Proceedings of Session 17B.2

Wednesday Morning, 17 August 1955

Chairman: **Mr. C. Eichner (France)**

Vice-Chairman: **Mr. R. Henych (Czechoslovakia)**

Scientific Secretaries: **Messrs. D. J. Dewar and R. Hara**

PROGRAMME

P/633	Techniques for manufacturing items of pure beryllium oxide for use in nuclear reactors	G. A. Meyerson
P/820	Status of beryllium technology in the USA	A. R. Kaufmann and B. R. F. Kjellgren
P/345	Sintering of beryllium oxide	R. Caillat and R. Pointud
P/1015	Purification of beryllium oxide	A. E. Cairo and M. B. Crespi

Discussion

Mr. G. A. Meyerson (USSR) presented paper P/633 as follows:

The chief quality required of beryllium and beryllium oxide is that they should be extremely pure.

To produce the purest beryllium oxide, a method has been developed in the USSR employing the well-known reaction by which the basic acetate of beryllium is formed. Industrial beryllium hydroxide is treated with acetic acid and the basic acetate formed is double-distilled at 360–400°C and then decomposed at 600–700°C.

Slide 1 (Table 1 of P/633) shows the impurity content in the original hydroxide and in the purified oxide, expressed as a percentage of the beryllium.

As will be seen from the table, the acetate distillation reduces the impurity content by several orders of magnitude.

Several methods have been developed for manufacturing articles out of beryllium oxide, varying according to the requirements they are to meet.

The simplest method is based on processes borrowed from ordinary ceramic techniques. A mixture of powdered beryllium oxide of various grades is pressed into graphite moulds and fired in them at 1800°C.

Under these conditions the articles produced have a density of about 2.1–2.2 gm/cm^3, or about 27% porosity.

Virtually non-porous and degasified articles are produced by hot-pressing the oxide under vacuum at 1850–1900°C and at a pressure of 15–20 kg/cm^2, or in some cases up to 50 kg/cm^2.

This high-temperature treatment under vacuum also has a supplementary purifying effect owing to the volatilization of the impurities.

There are two basic methods of producing metallic beryllium: reduction of beryllium fluoride by means of magnesium and electrolysis of fused beryllium chloride.

The raw material for the magnesium reduction method of producing beryllium from the fluoride is ammonium beryllium fluoride, which is converted into beryllium fluoride by calcining at 900–1000°C.

The magnesium reduction of the fluoride is done in graphite crucibles, heated by induction to 1300°C at the end of the reaction. The slag used is either an excess of beryllium fluoride or a mixture of beryllium fluoride and barium chloride (the latter reduces the beryllium content of the slag and hence increases the direct extraction of beryllium in the reduction process).

A purer metal is obtained by electrolysis. The raw material is beryllium chloride obtained by chlorinating beryllium oxide briquettes at a temperature of 550–650°C in tubular dies lined with quartz and heated internally by graphite electric heaters. The beryllium chloride vapour evolved condenses at 250–280°C in nickel condensers heated by hot air. The electrolysis is performed at 320–350°C from an electrolyte consisting of a mixture of beryllium and sodium chlorides with a beryllium concentration of about 6%.

At the low starting voltage (about 1.5 v), the impurities which are more electropositive than beryllium are electrolytically extracted, after which the cathode is changed and the voltage increased, and pure beryllium is deposited on the cathode.

The use of a changeable cathode means that the process can be made almost continuous, with very short intervals between cathode changes. The adoption of the preliminary stage of electrolytic refinement makes it possible to achieve a very high degree of purity in the metal, which is scarcely inferior in this respect to metal produced by distillation.

To free the beryllium, whether magnesium-reduced or electrolytic, from traces of volatile impurities, it is melted at 1500–1550°C under a low pressure of argon (about 20 mm of mercury). The maintenance of this low residual pressure is necessary to prevent any perceptible evaporation of the beryllium itself.

Beryllium of a high degree of purity is also pro-

duced by distillation under vacuum at 1300–1400°C (with a residual pressure of about 1×10^{-5} mm of mercury). Under these conditions the beryllium evaporates at the rate of about 0.3 gm per hour per cm^2 superficial area of the metal. The pure metal condenses in the heated zone of the condenser at 1120–1150°C.

Slide 2 (Table II of P/633) shows the change in the impurity content of the beryllium after distillation. It will be observed that this process reduces the impurity content by several orders of magnitude.

I must qualify these remarks by saying that the impurity content of the starting metal shown here is somewhat higher than that of the ordinary commercial quality produced by magnesium reduction from the fluoride. These figures refer to a starting metal produced from an ammonium beryllium fluoride solution which had not undergone supplementary chemical purification to free it from heavy metal impurities. This insufficiently purified starting material was deliberately chosen in order to demonstrate more readily the purifying effect of the distillation process. In the ordinary pure beryllium produced from the fluoride after proper purification of the ammonium beryllium fluoride solution, the heavy-metal impurity content is considerably lower than that of the starting metal shown here. The ingots made from melted beryllium have a heterogeneous, coarse-grained structure and are very brittle. Hence, if supplies of homogeneous, fine-grained structure are required, it is better to use powder-metallurgy methods. Beryllium ingots purified by melting are reduced to chips and then ground down to powder.

Depending on the requirements which the beryllium articles are to meet, several alterative techniques for converting the powder into dense bodies have been developed.

If articles of maximum density are to be produced from degasified metal, the method used is that of hot-pressing under vacuum in lined graphite dies heated by induction to 1100°C at the pressure of 50 kg/cm^2. Under these conditions a density close to the theoretical maximum is obtained.

Articles produced by this method are most suitable for use in high temperature work, if that is required; they do not become deformed or give off gases under such conditions and they are highly resistant to heat.

To avoid thermal stresses due to rapid cooling after hot-pressing, the articles are annealed under vacuum at 1100°C and slowly cooled.

The method used to produce articles of high density but for use in moderate temperature conditions is the simpler one of hot-pressing the beryllium powder or chips at 600°C in open dies made of heat-resisting alloys at a pressure of 5 tons per cm^2.

Articles of the same density but obtained from degasified metal may also be produced by first sintering under vacuum cold-pressed beryllium-powder briquettes and then subjecting the sintered product to calibrated hot-pressing at 600° in open dies made of heat-resisting alloys at a pressure of 5 tons per cm^2.

Finally, the simplest technique is used to produce articles in which some small residual porosity is permissible; the beryllium powder is pressed cold in steel dies at a pressure up to 15 tons per cm^2. The briquettes are then sintered in vacuum dies at 1150–1200°C, treated by calibrated cold-pressing and annealed under vacuum at 1100°.

Beryllium bodies produced by powder-metallurgy methods may also be used for extruding rod and tube at a temperature of about 500°C.

Here a cross-sectional deformation of 85% is permissible. The porosity of the extruded rod is less than 1%, i.e., it is close to the theoretical maximum density even when there was some residual porosity in the original material. Under test, the rod has been found capable of elongation by 5–10% in the direction of working.

With the various methods I have described of producing the oxide, the metal and articles made from it, it is now possible to transform a simpler and cheaper technology into a somewhat more complicated and expensive one, in order to satisfy the various possible demands on the quality of the products.

Mr. A. R. KAUFMANN (USA): summarized paper P/820 as follows:

It is well known that beryllium and beryllium oxide are materials of great potential value for nuclear reactors. They have not as yet, however, come into extensive use in the United States of America. This paper will describe the methods now in use for obtaining and fabricating Be and BeO and will outline the present understanding of their physical properties. Much progress has been made in producing these materials in satisfactory quality for reactor use.

At the present time commercial quantities of beryllium are produced only from the mineral beryl which is a beryllium aluminum silicate. The supplies of beryl are more than adequate for existing demand but it is to be hoped that cheaper sources of beryllium can be developed in the future. The chemistry of beryllium is widely known and all the commercial production is done either by a magnesium reduction of beryllium fluoride or by electrolysis of beryllium chloride. The details of these processes are of interest but there is not sufficient time in this talk to present many of them.

The first problem is to produce pure beryllium oxide from beryl. There are two methods in use in the USA both of which involve wet chemistry. The Brush Beryllium Company dissolves the beryl with sulfuric acid after a fusion treatment to open up the ore. This operation removes most of the silica and the aluminum is subsequently eliminated by crystallization of aluminum alum from the solution. The beryllium is then changed to sodium beryllate and finally is precipitated as hydroxide by heating the solution to 100°C. A chelating reagent is used to hold the heavy metal impurities in solution during this precipitation. The hydroxide is converted to oxide by calcining at about 1100°C. The Beryllium Corporation of America heats the beryl with various

fluorides in order to form sodium beryllium fluoride which may then be dissolved in water leaving the aluminum, silicon, and other impurities behind in insoluble form. Beryllium hydroxide is then precipitated by addition of caustic.

Both of these methods produce technical grade beryllium oxide at about the same cost. The sulfate method can be used to produce oxide of high enough purity for refractory and reactor use by a repetition of the process, but the fluoride method can only produce the technical grade of oxide.

Beryllium oxide may be fabricated into solid bodies for refractory and reactor use by a number of methods. For slip casting and dust pressing procedures it is desirable to use fused beryllia and to fire in an oxidizing atmosphere at about 1800°C. Calcined oxide may be used for hot-pressing in graphite dies at about 2200°C. The latter procedure yields bodies of full density.

Beryllium oxide is, of course, a brittle material subject to cracking under thermal stress. It has an unusually high thermal conductivity but this conductivity is substantially reduced by neutron irradiation. The thermal shock resistance may be improved by small additions of alumina or zirconia and by using a porous body. Extensive engineering tests have shown that beryllium oxide can be safely used in a low-power high temperature reactor but that further development is needed to make it satisfactory for a high performance reactor.

At the present time commercial quantities of beryllium metal are produced only by the Brush Beryllium Company using the magnesium reduction of fluoride. The first step in this process is to form a solution of ammonium beryllium fluoride from either hydroxide, oxide or scrap metal and then to remove heavy metal contamination, if it exists, by treatments with lead dioxide and with various sulfides. The pure ammonium beryllium fluoride is crystallized from solution and is then heated to about 1000°C to drive off ammonium fluoride. The fused beryllium fluoride is solidified and stored.

Reduction to metal is carried out in batches in a graphite pot at about 900°C. Only about 75 per cent of the stoichiometric amount of magnesium is used in order to keep the slag fluid at the end of the cycle. When the reduction is complete the temperature is raised to about 1300°C in order to melt the beryllium and allow it to collect in globules. The molten mass is poured from the pot and after solidification is broken up and washed with water to remove the slag. The final pebbles contain about 2 per cent slag, ½ per cent magnesium and ½ per cent of other impurities.

Melting of beryllium can best be carried out in vacuum using beryllium oxide crucibles. The use of vacuum leads to a removal of volatile impurities and thus a higher quality of metal. It is possible to make sound castings up to 8 inches in diameter and with good surface but this requires a very careful control of the melting and casting conditions. Up to the present time there has been little direct use of cast beryllium, the material being employed either for extrusion billets or for conversion to powder.

At this point it is desirable to discuss the physical metallurgy of beryllium in order better to understand the problem of making something useful out of it. Cast beryllium is almost hopelessly brittle. Many investigators have tried to remedy this condition by eliminating impurities, by trying to deoxidize the metal, and by adding alloying elements. None of these procedures has improved the ductility, and there is little hope that further effort will solve the problem.

It has been known for a long time that fabricated beryllium can display appreciable ductility in the direction of working. The explanation of this was learned recently through the discovery that single crystals of beryllium of commercail purity can exhibit large amounts of ductility in certain directions and are brittle in other directions. The plasticity is due to slip on $10\bar{1}0$ prism planes, while the brittleness is largely due to an easy fracture on the basal planes. Fractures can also occur on the 1120 prism planes and the $10\bar{1}2$ twin planes, but with greater difficulty then on the basal plane. Thus, it is clear that the preferred orientation in a polycrystalline sample of beryllium is important to its ductility.

Fine grained beryllium is usually more ductile than coarse grained material and therefore the recrystallization behaviour is of great practical importance. Recent studies have revealed that annealing of deformed beryllium occurs more commonly by polygonization than by nucleation of new crystals. For this reason it is difficult to get extensive grain refinement by deformation and annealing of cast metal. Fine grain size can be achieved in powder metallurgy beryllium because the oxide films on the original particles inhibit grain growth during sintering.

Let us turn now to fabrication methods for the metal. Due to the inherent brittleness it is necessary, even in hot working, to use special techniques which avoid tensile deformations. Extrusion is the best fabrication method for this reason. The beryllium metal, either in solid form or as powder, is encased in a thin shell of soft steel to prevent oxidation and to avoid sticking of the beryllium to the extrusion tools. A temperature of about 1000°C is best for extrusion but almost any other temperature can be used. Even at 1000°C the extrusion pressure is relatively high, and therefore only simple shapes such as rods, tubes and flats can be readily made. Hot rolling and forging can be carried out inside an iron sheath. It is almost impossible to cold work beryllium even after extensive hot working.

It should be clear from what has already been said that powder metallurgy is especially attractive for beryllium because of its ability to preserve a fine grain size. The process used by the Brush Company consists of converting vacuum cast metal to powder by machining it into chips and then by grinding between beryllium plates in a nitrogen atmosphere. The powder is sized to pass a 200 mesh screen. Consoli-

dation into bodies of essentially full density is accomplished by a number of methods. The best procedure to make large pieces consists of hot pressing at about 1050°C and at about 100 pounds per square inch pressure. Steel and graphite containers are used for this purpose. Good material can also be made by pressing at 1050°C and 1500 pounds per square inch without the use of vacuum. Small objects can be made by pressing powder at 150,000 pounds per square inch at room temperature, annealing at 1050°C, and then cold coining to size or, alternatively, by using this same pressure at about 500°C and then annealing at 800°C. All of these procedures yield a high density product of fine grain size, good machinability, and some ductility.

Now, let us return again to the matter of ductility in beryllium. It has been found by workers at the Massachusetts Institute of Technologoy and at Nuclear Metals Inc. that extruded powder beryllium can exhibit 20 per cent elongation at room temperature in the direction of extrusion and that cross-rolled powder can elongate as much as 40 per cent in all directions in the plane of the sheet. These results and those mentioned earlier can all be understood in terms of preferred orientation and grain size. It is clear that a specimen having a random orientation of grains should have low ductility since some grains will be oriented for easy fracture. Nevertheless, a fine grain size as in the pressed powders can lead to as much as 2 per cent elongation at room temperature. Extruded cast beryllium and extruded powder can be produced with identical preferred orientation, and yet the former has only about 3 per cent elongation while the latter has 20 per cent. This difference, presumably, is attributable to the relatively coarse grains of the extruded casting. The extruded powder is ductile in only one direction, while the cross-rolled powder not only has much greater ductility but also exhibits this in all directions in the plane of the sheet. In cross rolled material the basal planes are almost parallel to the sheet surface and therefore there are no planes of easy fracture perpendicular to stress in the plane of the sheet. In extruded powder the basal planes are randomly oriented about the extrusion axis and hence some crystals can fracture readily when the rod is stressed in a perpendicular direction. It is hoped that this one or two dimensional ductility in beryllium can find valuable use in the reactor field. It is clear, however, that these accomplishments are no substitute for true ductility such as is required of an engineering material.

The corrosion resistance of beryllium is worthy of mention. Commercial purity metal of high density is resistant to attack by air up to about 650°C. Corrosion at room temperature in moist air occurs only when excessive amounts of carbide or chloride are present. Attack by water at 100°C is extremely slow but at 350°C catastrophic corrosion often occurs. However, some samples are quite resistant to 350°C water and it is hoped that further research will produce material which is at least as resistant to water as is zirconium. Beryllium is not attacked by sodium at 500°C, but oxidation of the beryllium can occur if there is more than about 0.01 per cent oxygen in the sodium.

In conclusion, it seems appropriate to mention that health hazards exist in the handling of beryllium materials. Long experience has shown that workers in this field can be protected by proper attention to ventilation and cleanliness.

Mr. R. CAILLAT (France) presented paper P/345.

Mr. A. E. CAIRO (Argentina) presented paper P/1015.

DISCUSSION OF P/633, P/820, P/345 and P/1015

THE CHAIRMAN: Mr. Kaufmann asks Mr. Meyerson for more details on the method of decomposing the beryllium acetate.

Mr. MEYERSON (USSR): I will add some further details to what I have already said in reading the paper on the process of pure beryllium production by acetate distillation. Freshly-precipitated technical-grade beryllium hydroxide is treated with concentrated acetic acid to form the combination $BeO \cdot Be_3(CH_3COO)_6$. The basic acetate is then distilled at 360–400°C. This operation is repeated twice. This is of great importance in obtaining an extremely pure product. After double distillation, the pure basic acetate is decomposed at temperatures between 600 and 700°C. The result of this process is that finely-divided heavy beryllium oxide in very pure form, precipitates out of the gaseous phase. All of these processes are performed in gas-tight vessels connected together in such a way as to establish a continuous-flow process and also to prevent the penetration of volatile substances or dust into the working area occupied by the staff operating the apparatus.

One of the research objectives connected with this subject is, as in the case of various other metals which are to be protected against oxidation, to produce oxide films of complex structure which are more stable and homogeneous than the beryllium oxide which forms naturally on the surface of the metal. Research on these lines is still in progress at the laboratory stage; we are studying additions of various elements, such as nickel, aluminum, silicon, chromium, zirconium, etc., but so far we have reached no final conclusions as to which is the best substance to add. We have, however, observed one quite important fact that we thought was interesting to report to the conference. This observation is that the resistance of beryllium to oxidation is appreciably improved by means of additions even when the articles retain some residual porosity. In the case of pure beryllium, increased porosity sharply reduces its resistance to oxidation. As is mentioned in the text of my paper, however, it is possible by means of protective additions to raise the resistance to oxidation of even somewhat porous bodies close to the resistance offered by the densest and purest beryllium. We feel that this observation is of great practical im-

portance because it enables us to adopt simplified methods of producing beryllium articles while, as mentioned in the paper, achieving a satisfactory degree of resistance to oxidation.

The CHAIRMAN: Mr. Kaufmann's question is addressed to Mr. Caillat. He points out that in the United States the bricks are sintered at 2200°C and that this is necessary when the body is more complex than an ordinary brick.

Mr. CAILLAT (France): It is certainly possible to sinter the bricks under pressure at 2200°C. We preferred, however, to do it at 1850°C, but only for convenience. With regard to the manufacture of bodies more complex than a brick, to which you referred, I think, it is, of course, difficult to obtain highly concave shapes by sintering under pressure. However, my feeling is that this is more a mechanical difficulty in providing the plungers and dies than a difficulty that could be solved by raising the sintering temperature.

The CHAIRMAN: I have another question from Mr. Kaufmann concerning beryllium metallurgy. This one is addressed to Mr. Meyerson. Mr. Kaufmann would like to know what alloys are used to improve the resistance to oxidation of the beryllium.

Mr. MEYERSON (USSR): The determination by chemical analysis of the oxygen content of beryllium is, of course, very complicated. In our technological investigations we carried out comparative experiments, yielding rapid but perhaps not very accurate results, by using the well-known method of determining oxygen in metallic beryllium by chlorination, which yields a non-volatile residue in the form of beryllium oxide. Usually the oxygen content of beryllium depends not so much on the method of production as on the extent to which the metal has been reduced to powder form. For this reason we try to avoid extremely fine pulverization in reducing the beryllium to powder, and we find it possible to limit the oxygen content of the powder to rather less than 1 per cent, equivalent to about 1 per cent of beryllium oxide in the metal powder.

The CHAIRMAN: I should like to ask Mr. Meyerson a question myself: Have you determined the oxygen content of your very pure sublimed beryllium? In your paper you give the impurity content of sublimted beryllium. Is oxygen included?

Mr. MEYERSON (USSR): We have not observed any particular variation in oxygen content in metals of different origins once they have been reduced to approximately the same degree of pulverization. If the sublimated metal condenses in a compact form, its oxygen content will, of course, be lower than that of the same metal after pulverization.

Mr. TEMPLE (UK): I should like to ask Mr. Meyerson two short questions. Can you tell me the barium content of the beryllium, both before and after the vacuum melting, that is to say, beryllium produced by the magnesium reduction of beryllium fluoride?

Secondly, can you also give some idea of the beryllium content of the mixed barium fluoride flux, again after magnesium reduction?

Mr. MEYERSON (USSR): We have studied the use of an admixture of a barium salt as a flux in the magnesium-heat method of reducing the fluoride only during experiments which resulted in a certain additional technique designed to increase the direct extraction of beryllium, since the effect of the salt is to reduce the beryllium fluoride content of the slag. Subsequently, however, we found it possible to achieve good regeneration and complete recovery of the beryllium fluoride out of the slag and back into production, after separating it from the metal, so that there was no further need to investigate the technique involving an added barium salt. I mentioned it as one of several alternative techniques, but we have ceased to study it very closely; the result is that I do not at present have any further exact details, since the method not involving an added barium salt also proves to be reasonably economical if careful attention is given to regenerating the residue.

Mr. K. ALDER (Australia): The first question is rather a small point. Mr. Meyerson has mentioned the reduction of the fluoride and chloride content of beryllium by holding at a temperature of 1500°C. What crucible material does he use in this operation?

Secondly, Mr. Meyerson quoted some figures for the ductility of beryllium of 5–10 per cent. What fabrication process produces this ductility; and does he know of any process for the production of tubes with ductility in both the longitudinal and circumferential directions?

Mr. MEYERSON (USSR): With regard to the first question, concerning the temperature used in the magnesium reduction of beryllium fluoride, my colleagues have already informed me that they had heard an incorrect interpretation in which the interpreter gave the figure as 1500° instead of the 1300° quoted by me both in my oral statement and in the written text of my paper.

We raised the temperature to 1300°C in the reduction process.

With regard to the ductility of beryllium, I have already mentioned that rod extruded from material produced by powder-metallurgy methods sometimes elongates under tension by as much as 10 per cent. I have given an account of the conditions of extrusion in my statement and in the printed paper.

Mr. G. E. DARWIN (UK): I should like to ask Mr. Kaufmann if he could give us some further information on three points. He mentions in his paper that in stripping extrusions he uses strong nitric acid. Has he any information on the corrosion of beryllium which takes place during this operation and the effect of the strength of the nitric acid on this? Can he also tell us whether there is any hydrogen pick-up into the metal during this operation?

My second point is this: could Mr. Kaufmann elaborate on the effects of iron on the corrosion of

beryllium? I am particularly interested in gas corrosion. I notice that Brush Beryllium contains 1100 ppm. Does he consider this beneficial, or can he say whether it is beyond the beneficial limit? I notice in asking this question that Mr. Meyerson's beryllium only contains 300 ppm of iron, and I wondered if he had any further comments which would be of interest.

Thirdly, can he say anything about any work he has done on the welding of beryllium?

Mr. KAUFMANN (USA): With regard to the iron cladding of beryllium by nitric acid, we have not found that there is anything really critical about that. We usually use a 50 per cent nitric acid, but much stronger acid can be used except that the rate of dissolving of the iron is lower. However, I do recall that if there is a trace of sulfuric acid in the nitric acid, then it will attack the beryllium very readily.

We have never observed hydrogen pick-up as a result of this pickling operation; in fact, I am under the impression that hydrogen is insoluble in beryllium. We have not had any trouble which we have attributed to hydrogen pick-up.

My reference to improvement of corrosion resistance by iron was with regard to corrosion in water. We have note noted whether there was a corresponding effect with regard to oxidation. The amount of iron required to give this increased corrosion protection we are not sure of, but I think it is more than 0.10 per cent. The fact that there is about 0.10 per cent iron in the Brush Beryllium is merely because it does not seem worthwhile to reduce it below that, although I think that sometimes it does go down to as low as 5/100 per cent. There is objection to putting too much in beryllium because it makes it even more brittle than pure beryllium.

With regard to welding of beryllium, our work was done on extruded cast metal, and we found great difficulty in getting a weld which did not crack. There is no trouble in getting fusion, using the heli-arc. The oxide skin does not seem to interfere, but as soon as the arc passes by, a crack follows along behind. I think that welding of powder metallurgy beryllium can be done more readily, but we have not had occasion to do this.

Mr. R. K. HILTON (UK): Would Mr. Kaufmann care to indicate the order of magnitude of the change in thermal conductivity of beryllium with neutron irradiation at high temperatures, and what was the density of the sample to which his comment in the paper referred?

Mr. KAUFMANN (USA): I do not recall that these observations were made during irradiation at high temperatures. Perhaps there is someone here who would know. The magnitude of the reduction which occurred upon irradiation at low temperatures was about 50 per cent.

Mr. H. M. FINNISTON (UK): A considerable amount of work has been carried out on beryllium metallurgy in a number of countries—in the USSR, the USA, France and the UK, and it has been going on for many years. Is there any intention of using beryllium as a canning material in any reactor in the future, and, if so, in what sort of reactor and in what sort of conditions would this material be used?

Mr. KAUFMANN (USA): I believe the feeling in the United States is that beryllium has not yet been developed to the point where it could safely be used as a canning material. I did, however, notice in the French exhibit a piece of uranium canned in beryllium, if anybody wants to go and look at it.

Mr. MEYERSON (USSR): I should like to inform Mr. Finniston and other delegates who may be interested in this question that the Soviet Union is submitting a paper, to be presented by Mr. Morozov, on the properties of beryllium from the point of view of its use as a moderator in reactors. I imagine that this paper will provide some additional information on the question that interests you.

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